A STUDY OF THE THEORETICAL PRINCIPLES OF FROTH FLOTATION.

Being a thesis submitted by

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to the University of Glasgow in fulfilment
of the requirements for the Degree of Doctor
of Philosophy in Applied Science.

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May, 1949.

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ACKNOWLEDGMENTS.

The author wishes to acknowledge his indebtedness to Professor W.M. Cumming, O.B.E., D.Sc.,F.R.I.C.,M.I.Chem.E., F.R.S.E., Director of the School of Chemistry, for providing all the necessary facilities and for his help and keen interest in the investigation; to Professor G. Hibberd, Ph.D., A.R.T.C., M.I.Min.E., of the Mining Department, for the use of the Fagergren laboratory flotation machine; to I.A. Brownlie, B.Sc., Ph.D., for his help with the spectral work; and to the other members of the Staff of the Chemistry Department for their helpful criticism.

Thanks are also due to Mr R. Barbour for fabricating the various pieces of glass apparatus, and finally to the Department of Scientific and Industrial Research for providing financial assistance for the greater part of the time during which the work was carried out.

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Summary of Thesis.

The present state of knowledge with regard to froth stability is reviewed and its importance in the froth flotation process stressed. The bubble column is taken as the ideal froth flotation machine. The variables governing the formation of a dynamic column of froth are studied. The height of the column increases linearly with pressure of applied air and the resistance of the porous plate is always varying. The effect of change of temperature is greatest at low temperatures. Bikerman's law connecting froth volume with air flow is criticised. A new empirical law is suggested which provides constants for characterising froth stabilities. The froth column is subjected to dimensional analysis and two new equations are derived connecting height of froth column with air flow. The concentration of frothing agent for maximum froth stability is evaluated for the lower monohydric alcohols and the implications of the results discussed. The importance of Pine Oil as a flotation agent is analysed. The froth stabilities of aqueous solutions of three Pine Oil samples are compared with each other and with aqueous solutions of the chemical components of the Pine Oil complex. Terpineol, Borneol, Camphor, and Fenchyl Alcohol are true "frothers" and Anethole and Dipentene are "stabilizers". A stabilizer is believed to act through its ability to spread on the bubble wall. Flotation tests are carried out on a

Coal/Limestone mixture to compare the relative effectiveness of Pine Oil and its components. Traces of undissolved oil caused by adding the reagent dropwise to the flotation machine in moderate concentration gives increased recovery of Coal. Adsorption of frother on the Coal surface is suspected. The shape of the "recovery curve" in a batch flotation test is discussed.

INTRODUCTION.

The decision to undertake this investigation arose during an attempted separation of Ferrous impurities from lime and limestone by froth flotation methods. (1) As work progressed on that problem, it became increasingly clear that froth flotation methods had a more or less empirical basis and little or no theoretical background.

Although the first flotation patent was taken out as early as 1860 (William Haynes, E.P. 488; 1860), and the first workable froth flotation processes were patented around 1902, (Froment and Delprat Processes), research methods in this field today still consist for the most part of a trial and error search for new chemical reagents suitable for the separation of particular minerals. That these methods were not without success is evident from the fact that in 1931 up to forty one million tons of ore were treated by flotation in U.S.A. alone.

At first sight the process seems to be based on very simple and commonplace phenomena. A solid material, finely ground and suspended in water, is treated to make it non-wetted by the water, then brought into contact with a rising froth produced by some suitable reagent. Due to their non-wetting properties the solid particles pass partly into the gas phase, i.e. become attached to the bubbles of the froth, and in so doing are lifted to the surface of the froth where they can be removed by mechanical means. Thus two or more minerals can be separated by causing one to be preferentially non-wetted by water. The reagents used in the present day process are grouped under four main headings and are best defined by Wark (2). These are:-

(a) Frothers. A frother is a substance which, when dissolved in water, enables it to form a more or less stable froth with air.

(b) Collectors. A collector for any mineral is a substance (generally organic) which induces it to float at the air-water interface, and in the presence of a frother to form a more or less stable mineralized froth.

(c) Activators. An activator for any mineral is a substance (generally inorganic), the addition of which induces flotation in the presence of some collector that is otherwise without effect on the mineral.

(d) Depressants. A depressant for any mineral is a substance (generally inorganic), the addition of which prevents a collecto from functioning as such for that mineral.

This simplicity of the process has probably been its undoing, for physical chemists did not feel called upon to carry out research in a field where the mining and metallurgical engineer seemed to be so successful. As long as minerals could easily be separated by any one of a number of byproduct oils acting as collector, manufacturers were content to use that most easily available ..... and cheapest. As deposits thinned, however, and mineral mixtures encountered became more complex, the need for a more chemical outlook has become obvious, and the work of organic chemists and physical chemists has made itself felt in recent years in the application of flotation to the separation of closely related minerals, e.g. sodium chloride and potassium chloride crystals from their mixed saturated brine.

It will be found that most books on the process contain the statement that flotation is an art. This argument is based on the fact that the process involves the treatment of an ore, a natural product, and thus the mode of operation and reagents used must be modified to suit each particular ore. If, however, the process were thoroughly understood all that should be necessary, to indicate the nature of the reagents to be used, would be an analysis of the ore as regards constituent minerals and a determination of the ore texture to indicate the size to which the ore should be ground to liberate its mineral grains, i.e. into particles consisting of only one mineral.

The possibility of reaching this ideal state has provoked much excellent work. The voluminous literature of the American Institute of Mining and Metallurgical Engineers on flotation indicates the amount of present day research on the subject. In the hope of predicting a suitable collector for each mineral much fundamental work has been done on the mode of action of the collector. The leaders of this fundamental research have been Wark in Australia and Gaudin and Taggart in U.S.A. Opinion has been divided on the nature of the reaction between the minerals surface and the collector. The American school holds that the reagent functions by reason of chemical reactions of well recognised types between the reagent and the particle affected. Thus reaction depends on the solubility of the compound formed at the mineral surface between the reacting ion of the collector and the ion of opposite charge in the mineral lattice. It therefore appears that Sodium Ethyl Xanthate forms a stable coating on Galena due to the relative insolubility of Lead Ethyl Xanthate. The Australian school consider that the phenomena can best be explained in terms of adsorption. This can be physical adsorption or chemisorption. Thus the reaction between collector and mineral is a form of exchange adsorption and can take place in direct opposition to solubility product relations, e.g. Sodium Laurate adsorbs on Barytes in spite of the fact that Barium Laurate is about thirty times as soluble as Barium Sulphate. The flotation of such inert minerals as Coal, Graphite, and Sulphur cannot be explained easily by the chemical theory of Taggart.

Quite a few theories have been put forward in the past (3) on the physical aspects of the froth flotation process, but the majority of these suffered from the fact that they were not applicable to every case. Nowadays the field has grown so much that workers have become chary (4) of putting forward a comprehensive theory. Thus, although the chemistry of froth flotation is beginning to acquire a scientific basis, the physical aspects of the process have been a little neglected and are as yet imperfectly understood. This is largely due to the fact that a great number of variables govern the operation of a flotation plant, and each operator has to learn the caprices of his own mineral separation to achieve the best results. This has the effect of making a great amount of flotation research too applied, and the results of that research only locally applicable. To that extent froth flotation is still an art.

The physical aspects of froth flotation can be separated into two main topics. These are

(a) Froth formation and stability.

(b) Bubble-mineral adhesion.

They are independent of each other but may be together effected by some of the many variables of the process. Russian chemists have carried out much good work on bubble-mineral adhesion. This latter, however, is an extremely difficult field of research in which to obtain practical results consistent with theory, since the contact of a mineral particle in a flotation pulp with a bubble can only be discussed in terms of probabilities. It appeared to the author that there was more likelihood of obtaining useful results by attacking the first of the above two topics. The subject of this thesis is therefore a study of the factors governing the formation and stability of froth on a flotation cell, and an examination of the most commonly used frothing agent Pine Oil.

THEORY OF FROTH FORMATION.

The Froth.

If a bubble of air be introduced into a body of pure liquid it rises to the surface lifting a thin dome-shaped film of liquid above the surface level. This thins and breaks almost at once. If the life-period of this bubble be increased and a continuous stream of similar bubbles comes to the surface, the bubbles arriving first will be lifted above the surface on top of those following, and thus a rising mass of air cells, confined laterally by the walls of the containing vessel, is formed. Such a structure is generally known as a foam or froth. This increase in the life period of the bubbles can be produced by the addition of substances generally known as frothers to the liquid. Most soluble substances have some effect on the life-period of bubbles, but the most effective are surface-active organic materials, e.g. fatty acids, alcohols, etc.

Such a rising froth reaches its equilibrium level when the rate of production of bubbles equals the rate of destruction of bubbles, this latter always starting at the upper surface of the mass. As explained by Edser (5), the bubbles in a froth approximate in shape to rhombic dodecahedra, i.e. each cell has twelve approximately flat faces; the more similar in size the bubbles, the more plane the partitions between them, and the nearer is the ideal state of equilibrium reached. Since, however, there is a difference in pressure between the atmosphere and the topmost bubbles, their upper surfaces will be curved and an unstable state will exist which eventually leads to the rupture of the films.

Methods of Forming a Froth.

The bubbles of air which lead to froth may be introduced into the liquid in a number of ways. The simplest of these being the shaking of the liquid in a closed vessel which it only partially fills. This has its commercial counterpart in the mechanical agitation machine used in flotation practice, where a high-speed impellor churns air into the liquid. Taggart (6) has postulated that some of the bubbles so produced are the result of precipitation, due to the pressure difference across the impellor blades, of gas dissolved in the liquid. Gas precipitation is actually used in the Elmore type of flotation plant (7), where a mass of water is subjected to a sudden decrease in pressure, causing the gas in solution to be precipitated in the form of very small bubbles. Finally bubbles may be produced by passing air through a porous diaphragm into the liquid as is used in the Bubble-Column type of flotation machine, e.g. the Callow (8) and McIntosh (9) cells. This last method is perhaps the best for the study of froth formation and froth flotation generally, as the bubbles can be produced under known conditions of rate, size, etc.

Factors influencing Froth Formation.

Experimenters early found that not all liquids could be induced to froth. Pure liquids did not froth, and the froth forming capacity of solutions varied with the concentration of solute. Since some substances lower the surface tension of water, a low surface tension was at first thought to be a criterion of froth formation, due to the fact that a low surface tension should permit a large increase in surface area. On the other hand, a liquid such as amyl alcohol with a surface tension as low as 24.4 dynes per cm. froths no more than does pure water; and solutions of sulphuric acid and of some inorganic salts having a surface tension greater than that of water form froths to some extent. It is found moreover that although solutions of surface-active substances, i.e. substances lowering the surface tension of water, produce froths, saturated solutions of the same substances (with a still lower surface tension value) have little frothing power.

Although by 1873 Plateau (10) had postulated a relationship between the surface tension of a solution and the stability of its froth, Ostwald and Steiner (11) could find no correlation in experiments with humus sols, nor could Sauer and Aldinger (12) for solutions of various glues. Pankhurst (13) studied a number of frothers (wetting agents and gelatins) but could find no definite connection between froth stability and surface tension. Bartsch (14) on the other hand made a study of the frothing power of aqueous solutions of a wide range of frothing compounds and reached the following conclusions:-

(a) Aqueous solutions of all surface active substance, e.g. alcohols, acids, amines, etc., at relatively small concentrations show a maximum of frothing power .... saturated or supersaturated solutions of these substances have little frothing power.

(b) The influence of the surface activity on the frothing power is conditioned by the solubility of the solute. Thus, since in a homologous series the maximum solubility is reached by the lowest members and the maximum surface activity by the highest members (Traube's rule indicates that capillary activity increases as we ascend a series), for certain intermediate members there must be a favourable relationship between these two variables which makes them the best frothers, e.g., amyl alcohol, butyric acid.

(c) The surface tension corresponding to the concentration of surface-active substance for maximum froth stability is approximately constant and independent of the surface active agent.

(d) It is evident that the frothing power of a solution is influenced by the presence of a steep concentration gradient between the surface layer and the solution body as is suggested by the Gibbs' adsorption equation applied to solutions of surface active substances.

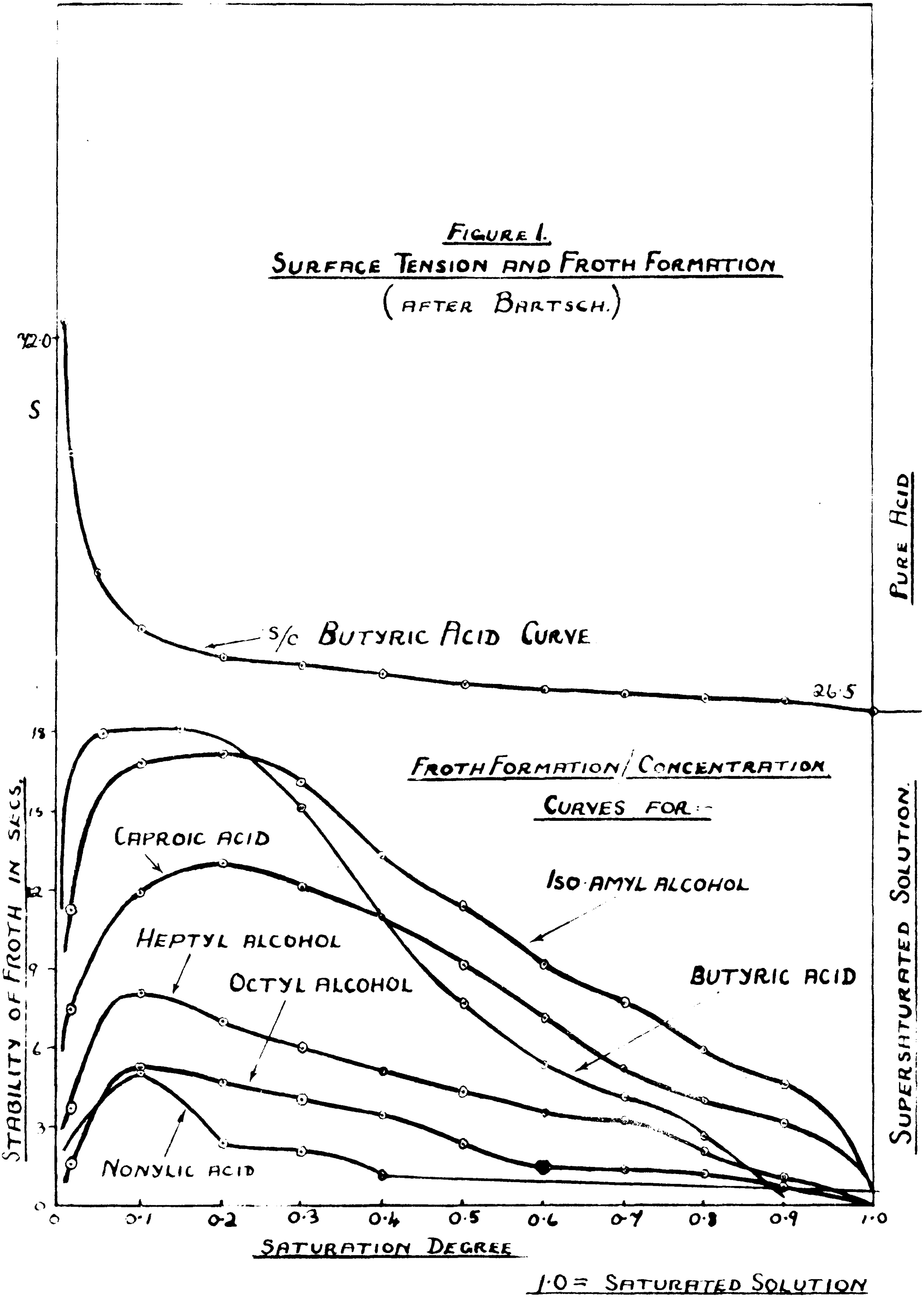
(c) High viscosity favours the stability of the froth system, but high viscosity alone cannot bring about froth formation.

By studying the froth stability in relation to the concentration of surface active substance, Bartsch found that as concentration is increased the stability increases rapidly at first, reaches a maximum, then falls more slowly. He gave the concentration corresponding to maximum froth stability for a large number of substances in water (15). The type of curve he obtained is shown in Fig. 1. taken from one of his papers (16).

Further to conclusion (b), Bartsch found that the addition of a second substance to the solution changed the frothing power in the same direction as it changed the solubility of the surface active substance. For instance, nonylic acid which frothed only very slightly in aqueous solution is a very good frother in 80% aqueous ethanol solution. In the same way the addition of a second capillary active substance may bring about a decrease in solubility so that the frothing power is impaired; for the addition of benzyl alcohol to solutions of isoamyl alcohol and of m-cresol was found to reduce their frothing power.

The tendency with workers on froth stability is, naturally, to make measurements on solutions forming very stable froths such as those for example from solutions of albumin and saponin. Such solutions, however, have been

FIGURE I.
SURFACE TENSION AND FROTH FORMATION
(AFTER BARTSCH.)



shown to have a high surface viscosity which is evidently due to the irreversible adsorption of the solute at the interface to form an ultra-stable film. Thus surface tension lowering alone could not account for the froth stability of such solutions. On the other hand all the substances tested by Bartsch were of fairly low molecular weight and the solutions could be said to have little or no surface viscosity.

In using Gibbs' adsorption equation to explain frothing power Bartsch was only following a number of investigators who had already reached the same conclusion. In 1876 J. Willard Gibbs (17) proved from thermodynamic considerations that, if the addition of a solute lowered the surface tension of the solvent, there must be excess of solute at the surface of the solution such that:-

$$U = \frac{-c}{RT} \cdot \frac{ds}{dc}$$

where c is the concentration of the solution, R the gas constant T the absolute temperature, and $\frac{ds}{dc}$ the rate of change of surface tension with concentration. Since, on the addition of organic surface-active substances to water, $\frac{ds}{dc}$ is negative (see the upper curve of Fig. 1), U is positive, i.e. there is an excess of solute in the surface layer. In the case of inorganic salts the surface tension is raised slightly and U becomes negative. This equation has been tested experimentally by many workers. Discrepancies have been found in the case of substances forming definite films on water, but this has been explained by the fact that Gibbs was considering only an equilibrium state where the concentration at the surface was thermodynamically reversible, whereas surface films of such substances as saponin and albumin (18) and sodium glycocholate (19) do not come strictly under this heading, since, as explained above, adsorption of such large molecules at a water surface tends to be irreversible. Otherwise, the equation is well supported by experiment. Referring again to Fig. 1, it can be seen that the maximum frothing power coincides with a high negative value of $\frac{ds}{dc}$ and thus the concentration difference in the boundary layer has a relatively high value. Edser attempted to explain frothing in terms of this slope of the curve of surface tension against concentration, but Shorter (20) went further and postulated the existence of a surface "pellicle" formed from the molecules of dissolved substance and solvent which leads to frothing ability. He also ascribed the maximum frothing power to a certain degree of heterogenity of the surface layers with reference to the molecules of solute and solvent, i.e., at infinitely small concentration of solute the Gibbs' layer is composed of water molecules and at infinitely high concentration of solute that layer consists of molecules of surface active substance. At the two extremes the boundary layer is homogeneous with reference to the types of molecules, and the frothing power is low. Between these two values the layer becomes heterogeneous and foaming occurs.

Foulk (21) developed Edser's argument a stage further in the following manner. He considered the formation of a liquid film due to two bubbles approaching each other under water. If the water be pure then the bubbles on approaching very near each other will coalesce, that is to say, there will be no resistance to the indefinite thinning of the film between the bubbles. In the case, however, of a solution of a surface active substance there will be obtained a concentration excess at the bubble surface and this will give rise to two forces in equilibrium, viz., the diffusion pressure tending to force the adsorbed molecules back into the body of the liquid and the force of adsorption holding them in the surface. Now if the two bubbles were to approach beyond a certain distance there could no longer be a concentration gradient between the surfaces and the centre of the film, and to achieve this state work would have to be done against the force of adsorption .... thus the motion of the bubbles is stopped. Edser puts it as follows:-

"When the bubbles begin to approach each other, a change occurs in the molecular forces producing the local concentration, with the result that the osmotic pressure becomes unbalanced, and the unbalanced force will tend to stop the motion of the bubbles."

The Nomenclature of Frothing.

At first sight it seems almost impossible to separa the terms frothing power and froth stability, because in every case the former is the result of the latter. But it is important that we should understand the difference between them to get a clear insight into the theory of frothing. Most workers in measuring frothing power, frothing capacity, frothing ability are really measuring froth stability. Even in cases where the volume of foam produced by some standard agitation method is measured at a definite time after cessation of shaking, this is only possible through the high froth stability of the solution.

Let us now try to define these terms more clearly.

The Frothing Capacity of a solution is controlled by the factors influencing the initial formation of froth, i.e. it is really the latent ability of a given solution to form a froth.

The Froth Stability of a solution is controlled by the factors influencing the life period of the bubbles making up the froth after its formation. It is the period of time which is the total life of the froth from its formation to the bursting of the last bubble.

The term Frothing Power has no exact definition. It is the direct result of the complementary action of frothing capacity and froth stability, and is proportional to the amount of froth formed under any given set of conditions.

Factors influencing Frothing Capacity.

According to these definitions the frothing capacity of any solution must be theoretically proportional to the decrease in free surface energy produced by the adsorption of the solute at the surface, i.e. the change in surface tension from that of a newly formed surface of the solution (Dynamic Surface Tension) to that of the surface after equilibrium adsorption of the solute (static Surface Tension). With most solutions the adsorption process is so rapid that it is very difficult to measure the surface energy at zero time (t_o) but with a solute of comparatively large molecular dimensions equilibrium is established more slowly and we may approximate to the value at time t_o. In the case of a pure liquid with a high surface tension like water or a low surface tension like amyl alcohol the surface tension is a constant quantity and there is no frothing capacity.

Where we are dealing with two liquids completely miscible in all proportions, such as ethanol and water which have a surface tension/concentration curve falling nowhere below the surface tension of the pure alcohol, it is uncertain, after a certain solution concentration of alcohol in water is reached, whether it is more correct to say that the alcohol is lowering the surface tension of the water or the water is raising the surface tension of the alcohol. Thus it is, that near the pure alcohol end of the concentration scale we have the phenomenon of a solution that froths and yet has a surface tension greater than that of the pure solvent (ethanol). We are therefore now able to bring into line the frothing of solutions of inorganic substances such as sulphuric acid which have a surface tension greater than that of water. There is still a change in free energy from the dynamic to the static surface tension. Thus we should consider the change in surface tension of a solution with reference to its dynamic value and not with reference to the surface tension value of the pure solvent.

This loosening of the surface, if we may be allowed so to call it, is the frothing capacity.

Foulk (20) showed experimentally that for solutions of sulphuric acid the frothing power was greatest when the difference between the measured static and dynamic surface tensions of the solutions was greatest. His frothing measurements, however, involved froth stability rather than frothing capacity.

An attempt has been made here to show frothing capacity graphically. As shown in Fig. 2. PRQ is the normal surface tension/concentration curve for a two component system such as ethanol/water. PSQ is the hypothetical surface tension/concentration curve for the surface at zero time (the dynamic surface tension). This cannot be measured experimentally, so in taking a straight line relationship we are only considering the simplest case possible. Association of either component would probably change the shape of

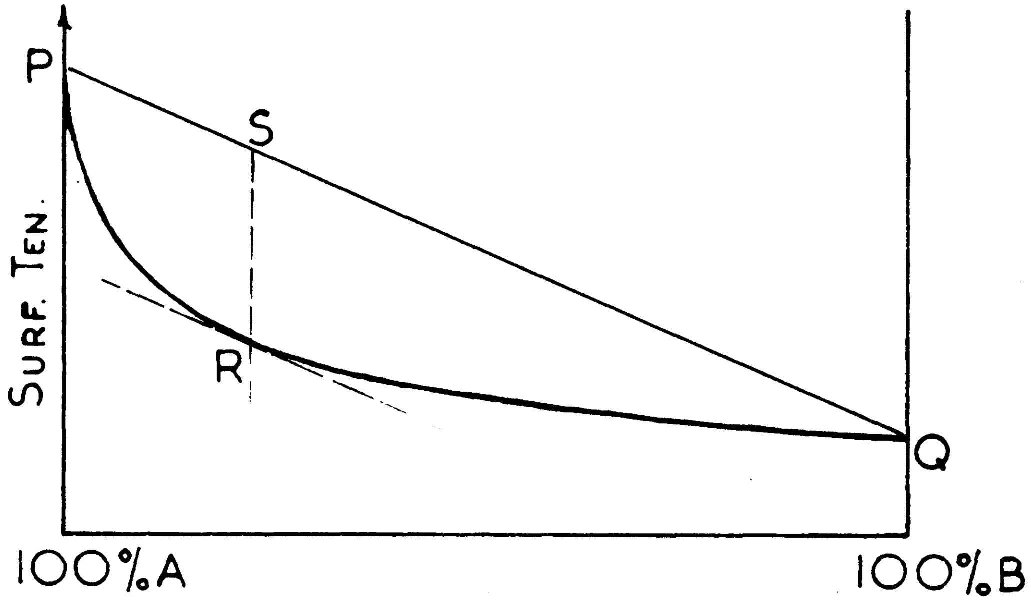


FIGURE 2

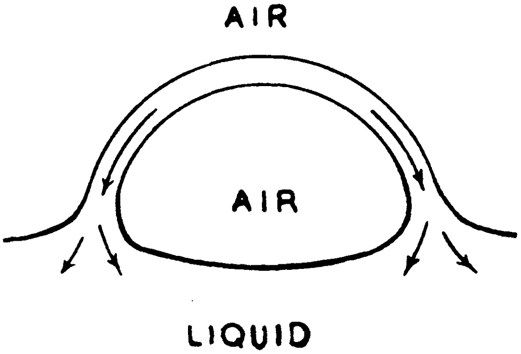


FIGURE 3

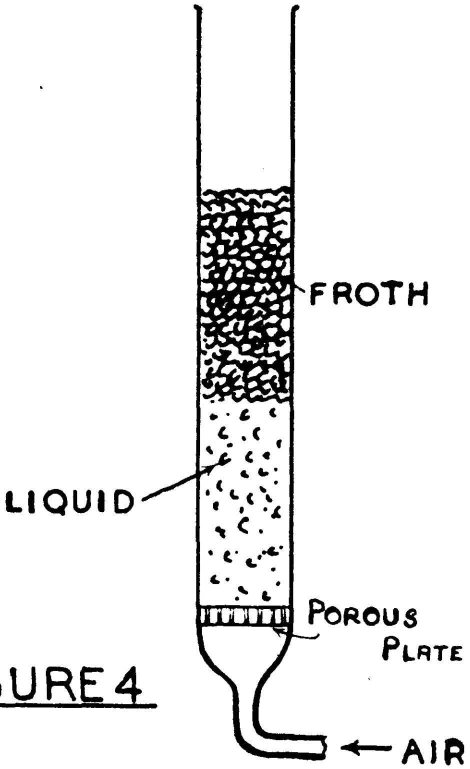


FIGURE 4

BUBBLE COLUMN

the curve. The vertical distance between the two curves at any point is thus a measure of the frothing capacity. Thus point R where the tangent to PRQ is parallel to PSQ corresponds to maximum frothing capacity.

Factors influencing Froth Stability.

The amount of froth produced from a solution is dependent finally on its stability. Thus it becomes possible that a solution may potentially have a relatively high frothing capacity yet produce very little froth in practice if the stability of the froth is very low. This is recognised in froth flotation practice where substances known as stabilisers are added to the pulp of ore and frothing solution to increase the life of the bubbles in the froth.

Froth stability is a much more tangible quantity and can be measured in a number of ways.

The best idea of the factors involved in the stability of a froth can be obtained by studying the forces at work towards the destruction of a single bubble at the surface of a liquid shown diagrammatically in Fig. 3.

The forces are:-

(1) The force of gravity tending to drain liquid from the film back into the body of liquid.

(2) The surface tension force tending to prevent stretching of the film.

(3) The viscosity of the liquid in the film tending to prevent drainage, and the thinning of the film.

(4) Local forces, e.g., thermal agitation of the molecules of the film.

e.g., mechanical agitation of the film by outside sources.

e.g., evaporation of surface active molecules from the film.

Perhaps the most important of these is (3), but it is doubtful when dealing with such thin films, whether we are encountering the same viscosity of the liquid as it has in bulk, particularly since there are zones of high concentration of adsorbed molecules associated with the bubble surfaces. In such a film the force of friction must be great, because, according to the law of Poiseuille the speed of liquid movement in a capillary varies as the fourth power of the radius.

Gibbs (23) obtained an equation for the mean velocity of water falling between parallel plates, viz.,

$$V = 899\ D^2 \text{ ---------------------- } (1)$$

where D is the distance in mm. between the plates,

and V is the mean velocity of flow in mm./sec.

Ross (24) used this equation to derive an expression for the drainage from a liquid film under the action of gravity, relating the volume drained with time.

This proved to be:-

$$\frac{V_0 - V}{V_0} = \frac{1}{(bt + 1)^{\frac{1}{2}}} \text{ ----------------(2)}$$

where $b = 2\left(\frac{899\ D_0^2}{l}\right) \sec.^{-1}$

and V_0 is initial volume of liquid in ccs. in film.

V is volume drained out in time t secs.

D_0 is initial thickness of film in mm.

l is the vertical height of the film in mms.

Though this was an advance the results could not be applied to the more or less complex froth system.

Using Poiseuille's law for the drainage of liquids through vertical plates, i.e.

$$-\frac{dV}{dt} = \frac{b.g.a^3\rho}{12\,\eta} \text{ ---------------------- (3)}$$

where b = herizontal dimension.

g = gravitational constant; ρ = density of liquid.

a = thickness of film; η = viscosity of liquid.

V = volume of liquid in film.

Brady and Ross (25) derived an equation in which the foam column was considered to be made up of a series of vertical films, and introduced the conception of limiting thickness of film below which the film would no longer thin due to drainage, but would rupture.

This equation was,

$$t_1 = \frac{6\,\eta A}{g\rho} \times \left(\frac{1}{a^2} - \frac{1}{a_0^2}\right) \text{------------(4)}$$

where t_1 is the time required for first film at top of foam mass to rupture.

A is the height of the film.

a_0 is the initial thickness of the film.

a = final limiting thickness of the film.

Further, it was found by applying this equation that L_g, the average life of gas in the foam, was given by the expression,

$$L_g = \frac{\eta h_0}{\rho} \times K\theta \text{ ---------------------- } (5)$$

where h_0 is initial foam height, K is a constant; and θ is a complex function of the limiting foam density, i.e.

$$d = \frac{V_1}{V_g + V_1}$$

where V_1 = volume of liquid and V_g = volume of gas in foam

This equation applies only to a static foam height and idealized foams.

Starting from the same Poiseuille equation, No. (3), Constable and Reizi (26) considered the case of drainage from a hemispherical film as covers a bubble at a water surface, and derived an expression like equation No. (4) above, viz.,

$$\frac{1}{a^2} - \frac{1}{a_0^2} = \frac{g\rho t}{3\eta r} \text{ -------------- } (6)$$

Where the symbols have the same meaning as for equation No. (4) and r = radius of curvature of hemisphere, and considering that (a_0) is much greater than (a) this becomes

$$t = \frac{3\eta r}{g\rho a^2} \text{ --------------------------- } (7)$$

Experiment showed however that the bubbles seemed to drain faster than required by the equation. It appeared from their experiments that the local forces in a froth far outweighed the normal drainage, in that the collapse of each bubble in a froth gave a shock to all the others and since small bubbles are less affected by this than large, they have a greater chance of remaining upruptured. Since also the probability of rupture of a bubble is proportional to its exposed area, big bubbles will tend to collapse sooner than small. These points prevent the above equation No. (7) from holding experimentally and serve to show the difficulty of applying mathematics to a complex froth. It is not clear whether we should keep the bulk viscosity in such equations or replace it by a form of superficial viscosity.

It should be said with regard to the effect of surface tension on the stability that the inherent variability of the surface tension of such solutions plays a part in the stabilizing of a froth. For if a film is stretched after reaching the static surface tension, liquid from the inner part reaches the surface and the concentration of solute on the surface is lessened with a resulting increase in surface tension which counteracts the force tending to break the film.

The Orientation Theory.

The discussion of films brings us to a study of the influence of the configuration of the molecules involved in forming bubble films. According to the Langmuir-Harkins adsorption theory surface-active molecules at a solution surface have always a definite direction of orientation.

It was during work with films of oleic acid on water that Lord Rayleigh found that there was no fall in surface tension until a certain concentration of oleic acid was reached. This led to the discovery that the film in this condition was one molecule thick. Hardy (27) while working on the lubrication of surfaces with oil films suggested that the molecules in such films must be oriented in a specific direction. Langmuir studying monomolecular films on water propounded his theory of residual affinities by which he explained the difference between the solubilities of fatty acid films and those of the corresponding hydrocarbons. According to this theory a molecule of fatty acid on a water surface is attracted in such a way that the carboxyl group (a so-called hydrophilic or polar radicle) turns towards the water molecules and the methyl chain (hydrophobic or non-polar radicle) is repelled in such a way that the molecule stands with its long chain more or less normal to the water surface. Thus the thickness of the film when the molecules are closely packed is just the length of one molecule of fatty acid. Harkins came to the same conclusion as Langmuir from a different angle. Making a study of the mutual attraction ($\Delta\sigma$) of liquid surfaces, he evaluated the separate surface tensions of the liquids and their interfacial tensions when in contact. It was found that the greater the attraction the greater the mutual solubility, but, that for a given homologous series the value of $\Delta\sigma$ became nearly constant from the four carbon-chain onwards, but the solubility continued to diminish rapidly. The conclusion was therefore reached that the value of the attraction was due to the characteristic group of the series, e.g. alcohols.....hydroxyl, acids..... carboxyl, and the decrease in solubility to the increasing length of the carbon chain. Thus a film of such molecules on water would be so arranged that the characteristic group was in contact with the water surface.

Turning now to surface active substances soluble in water and which do not form insoluble surface films, we would expect that such molecules would orient themselves in much the same way on adsorption; of course in this case they must be more or less hemmed in by water molecules rather than standing free on a water surface as in the case of an insoluble film. This is supported experimentally by work by Dervichian (28) on the lower members of the fatty acid series.

It seems therefore that to have a particular degree of stability froth films constructed from soluble surface active molecules must have a definite architecture. The "bricks" for the structure being surface active molecules and water molecules in a definite proportion. This is not unlike the heterogenity principle postulated by Shorter. Since the surface active molecules are completely soluble in water the adsorption equation of Gibbs should be applicable in determining the concentration of surface active substance in the surface at equilibrium.

Other Factors in Stability.

In the complex pulps of flotation practice there occurs other materials in the bubble films. These include electrolytes, solid mineral particles, and colloids.

Bartsch studied the action of electrolytes on the stability of various froths and found that they are effective in the same way as they are on lyophobic sols. Precipitation or decrease of solubility of the froth agent by the addition of the electrolyte causes a decrease in froth stability. Protective colloids can be employed to prevent precipitation in the usual way. Used at low concentration they increase the stability of the foam since they are generally surface active substances. If solids, however, are present in the bubble films high concentrations of protective colloid can displace the solid phase completely from the foam system with a resultant loss in stability. This property of colloids finds practical use in the flotation industry for the separation of minerals.

A high rigidity of the bubble film may have a bad effect on its stability, particularly under the action of the local forces mentioned above. Thus saponin solutions form rigid bubbles and the addition of soap solution to the films is found to increase the elasticity and the stability. Similarly it is well known that the addition of glycerol to soap solutions assists in the formation of soft and flexible films not easily ruptured under stress.

Solids have only a stabilizing action on the bubbles if they are actually on the bubble wall, i.e. at the air/soln. interface, in a condition to be floated. The froth in this condition is said to be mineralized and has an enhanced stability. The degree of stabilizing produced depends on the quantity and quality of the solid in the film. The quantity refers to the percentage of the total bubble wall that is covered by mineral; the quality refers to the fineness of the solid particles and their shape. Thus the more completely the bubble is covered by solid material the greater is its stability. As far as fineness is concerned, Bartsch found that the stability passed through a maximum with progressive reduction in size and fell again when colloidal dimensions were reached.

Summarizing then the factors influencing froth stability we have:-

(a) The production of Gibbs' adsorption layer.

(b) The shape of the surface active molecule with regard to its effect on the superficial viscosity, and with reference to its orientation at the surface.

(c) The proportion of surface active molecules in the film producing the degree of saturation of the interface requisite for maximum stability.

(d) The action of electrolytes in precipitating or changing the solubility of the surface active substance.

(e) The action of protective colloids both as surface active agents and as destabilisers in the removal of solid from the froth.

(f) The action of solids in a qualitative and quantitative sense.

It is obvious that the froth stability can play a great part towards the success or failure of any froth flotation process. This is discussed from a practical point of view by Gaudin in his book "Flotation" (29). The characteristics of a "good" froth in flotation practice, or the maintenance of a mass of air bubbles with definite properties above the surface of the pulp have a purely empirical basis. Thus in the literature on froth flotation we see the descriptive terms, "tough", "brittle", "dry", "voluminous", "stiff", "soapy", applied to froths. A good froth should be stable enough to carry the mineral load, but not so persistent or "tough" that it remains, after it leaves the cell and passes over into the collecting vessel. Bubbles should be small; and there should be rapid break of bubbles at the top of the froth so that the mineral load is momentarily transferred to lower bubbles. In this way further classification takes place and entrained gangue particles get a final opportunity to drain back into the body of the pulp. When the flotation agent is of an oily nature, brittle froths having low carrying power are produced at low concentrations of oil, while "overoiling" or high concentrations of oil tends to produce tough films which hold solid tenaciously.

Thus the "frother" must have a duplex character; i.e. it must first be surface active, lowering surface tension to cause bubbles to form and providing a large enough non-polar group to give the film the required degree of stability, but secondly it must be able to modify the stability of the film so that it becomes resistant to mechanical shock, bending stress, rapid stretching, etc. The bubble film must have more of the nature of a flexible membrane. This second characteristic can be provided by an oil. Very few surface active compounds combine both features; thus most practical frothers are mixtures. Using a surface-active material alone tends to produce a brittle froth, e.g. the froth produced by solutions of amyl alcohol in water. Increasing the size of the non-polar group, e.g. Oleic acid, helps matters somewhat, but the results are offset by the resultant decrease in solubility with a corresponding detrimental effect on the frothing power. If we attach to the molecule a more powerful solubilizing group and form a soap, say, e.g. Sodium Oleate, or a detergent, e.g. Lauryl Sulphate, we obtain a tough soapy film which at high concentrations of reagent seems to be armoured against the entry of solid, and the mineral load is decreased. The exact nature of this armouring phenomenon is not as yet understood (30), but it seems to be associated with the formation of a rigid matrix of frother molecules in the bubble film. The dry brittle froths produced by solutions of saponin are also of this nature.

The addition of a pure non-polar hydrocarbon oil to water produces no froth on agitation. In actual practice, however, most mineral or vegetable oils contain quantities of oxidised material whose polar nature tends to make the oil a frothing agent. If we mix with the oil a further proportion of a surface active agent we obtain a reagent whose properties can be modified to suit the type of froth required as described above. The mode of action of the oil in modifying the properties of the bubble film is bound up with its surface-viscosity. In the same way, if the surface active agent has an affinity for the mineral surface, i.e. is a collector for the mineral, the addition of the oil causes the film on the mineral surface to be more stable and continuous, with a resultant increase in the contact angle and recovery of mineral. We have examples of such compound frothing agents in both the natural and synthetic reagents.

Among the natural reagents we have,

Tar oils from Coal or Wood.

e.g. Barrett No. 4, (coal tar creosote oil) containing neutral oil and surface active tar acids.

e.g. Pine Oil or Eucalyptus Oil, containing terpene hydrocarbons and surface active terpene alcohols.

Among the synthetic reagents we have,

e.g. Cyanamid Co. Frothers 52, 58, and 60, containing proportions of the higher aliphatic alcohols and fuel oil.
e.g. Flotal, a synthetic mixture of alcohols and terpene-type hydrocarbons (similar to Pine Oil).

In the search for better reagents further mixtures are sometimes used, e.g. Creostoe-Pine Oil mixtures, Frother 60 - Pine Oil mixtures.

Experimental Methods of Making Froth Measurements.

An excellent review of this part of the subject is given by Ross (31).

The best division of the methods is into static and dynamic methods. Static methods are those in which measurements are made after the froth has been produced. Dynamic methods are those in which measurements are made during the formation of the foam, usually by a current of gas passing through the liquid. The static methods are most suitable for high stability measurements and the dynamic for low.

Under the heading of static measurements perhaps the most obvious is the measurement of the life period of single bubbles at the surface of the solution, after they have been produced under standard conditions. Such a method can be very unreliable because of the difficulty of producing standard bubbles. The chief difficulty is that of keeping a quiet solution surface uncontaminated or at least contaminated to a reproducible degree. This was attempted by Hardy (32), Talmud and Suchowelokaja (33), and E.E. Wark (34). The reliability of the method is such that only general trends can be discussed rather than definite conclusions.

The agitation method, also static, has been very popular in the past and in its simplest form consists in the shaking of a vessel containing the solution under more or less standard conditions, and taking the time from cessation of shaking to total collapse of froth as a measure of the stability. Although the method is rather crude, where the investigator has a certain amount of patience and is willing to repeat the test till reproducible results are obtained, quite an average degree of accuracy can be achieved. All Bartsch's results mentioned above were obtained by this method. Alejnikoff (35) made a critical study of the method but abandoned it in favour of the bubble column. The accuracy of the method varies with the stability of the froth and should only be used for stabilities of more than, say, thirty seconds. If the shaking is carried out by hand the amount of froth formed is largely controlled by personal vigour, time of shaking, heat from hand reaching containing vessel, etc. After a certain amount of shaking has taken place, further shaking partly breaks up the foam first formed. Sasaki (36) however, in confirming some of Bartsch's results used the bubble column method, but later employed a mechanical shaking apparatus to study the frothing properties of a number of ternary systems.

The last bubbles to disappear in a static collapsing froth column are those around the edge of the clear liquid meniscus against the vessel wall. These appear to have an enhanced stability due to the proximity of the wall. If the time of collapse is taken to include the disappearance of these bubbles one gets rather erratic results particularly for froths of low stability. This can be avoided by the method of Constable and Erkut (37) who took the time for the froth to settle until the first sign of a clear liquid surface appeared. The bubbles round the edge of the surface were ignored.

Arbuzov and Grebenshchikov (38) produced froth by sucking drops of liquid through a porous disc where air was taken up and froth produced. The froth was collected in a measuring vessel. They maintained that methods where the foam remained in contact with the liquid from which it was formed gave erroneous results since the liquid is at first depleted of surface active substance and it is thus sometime before equilibrium is reached.

Most of the dynamic methods utilise the bubble column (or Dynamic Foam-meter) used by Foulk and Miller (39); Alejnikoff; Lederer (40); and Bikerman (41).

This apparatus is depicted in its simplest form in Fig. 4. and consists of a long tube with a porous diaphragm at the base through which air is passed. The liquid to be frothed is put in the tube and the air pressure raised to a constant level. When equilibrium froth height is reached measurements are made. Some workers have taken the time for the froth to reach its maximum height as a measure of stability but this has been shown by Lederer and by Ross to be really only a measure of the inflow rate of the air. This instrument has the great advantage that it has a counterpart in the flotation industry in the Callow cell and its variations pores in action giving a constant average value which is a good approximation to an isoporous diaphragm.

Since the method of the bubble column seemed the most likely to produce reliable results, and since the solutions likely to be encountered would be of fairly low stability, it was decided to use an apparatus of this form. The industrial counterpart of this apparatus is the most useful for making complex separations, thus it was felt that a study of the principles involved in its operation would be of great interest.

The First Frothing Apparatus.

Before designing a frothing apparatus a study was made of that used by previous workers and the following conclusions were reached. The apparatus should have -

(1) A convenient air supply.

(2) A filtering system for the air.

(3) A pressure gauge for the air.

(4) A means of supplying solutions free of contamination.

(5) A means for easy removal of solutions.

(6) A frothing tube of convenient length fitted with a sintered glass disc for producing the bubbles.

All of these were included in the apparatus designed and built. It is shown in Fig. 5 and photograph 1.

(1) The air supply first used was that available in the laboratory from a supply tank and compressor. The supply pressure varied from zero to 40 lbs/sq. in. depending on when the compressor was last run, and was controlled by a needle valve. It was soon found that not only was this control not fine enough but that if a further valve (screw clip) was fitted at some convenient point in the apparatus, the whole supply pressure was apt to be thrown on that portion of the apparatus before the screw clip with disastrous results. A spring loaded reducing valve designed to drop the pressure to 2 lbs/sq.in. wad installed. This pressure was too low to operate the apparatus, and adjustment of the spring loading

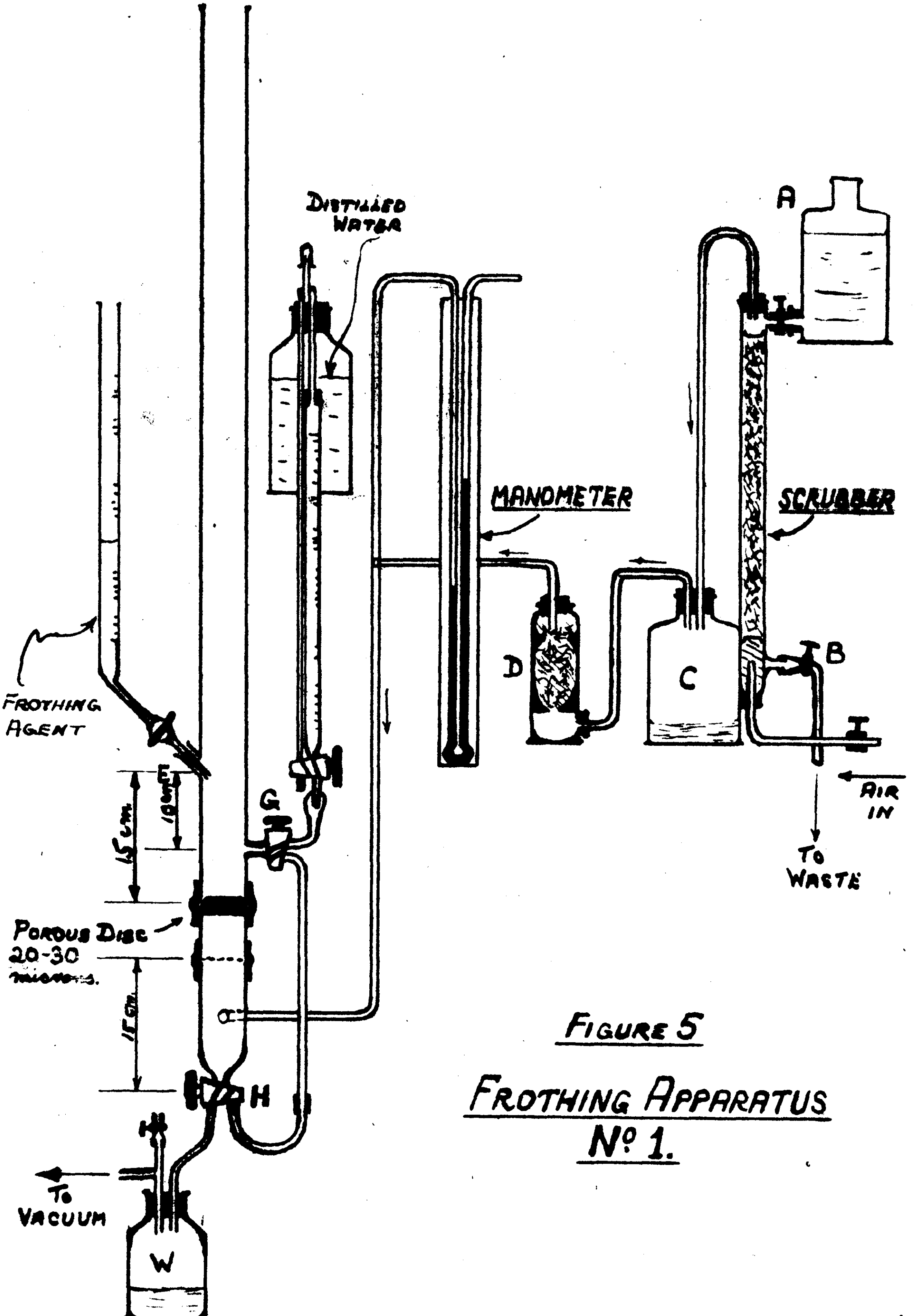


FIGURE 5

FROTHING APPARATUS No. 1.

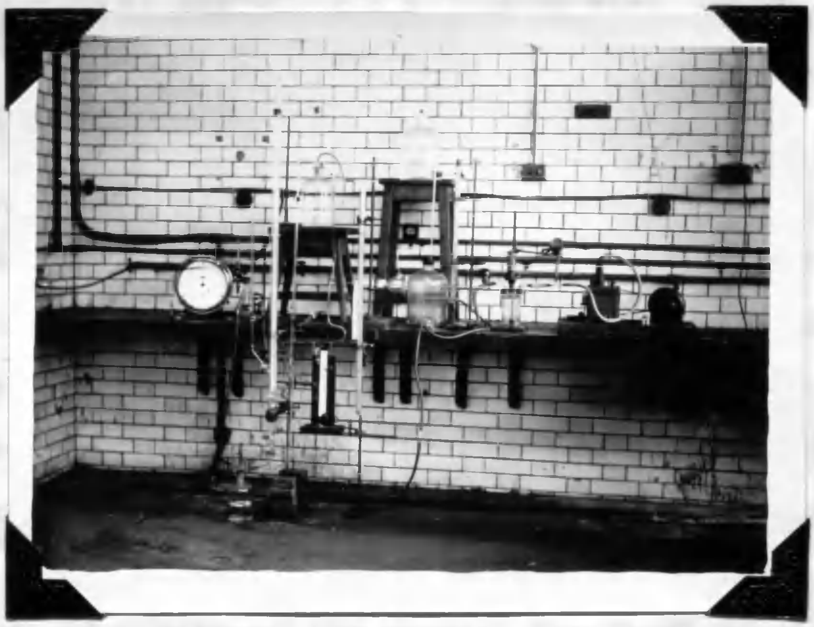


Photo. 1.

Frothing Apparatus No. 1.

The clock-face to the left of the frothing tube is that of the wet gasmeter used to calibrate the air flow meter on the lower right of the frothing tube.

device was found to be tricky and the spring apt to stick on sudden loading of the high pressure side so it too was discarded. It was decided to use an independent air supply and this was finally derived from a motor driven rotary oil vacuum pump by connecting the exhaust side of the pump to the apparatus. It was found that the pump would continue to operate with more than ten lbs/sq.in. back pressure on the exhaust side. The volume rate of air being supplied by the pump was found, however, to be larger than that normally required and that fitting a clip in the supply line to throttle the air flow rate increased the back pressure till the pump shut down. This also occurred when the reducing valve was fitted to the exhaust side of the pump. The final arrangement used is that shown in the diagram (Fig. 6.) and has never given further trouble. The main part of the device is a spring-loaded safety valve which acts as a bleed-off for the excess air and keeps it at a more or less constant pressure as indicated by the supply pressure gauge. The valve is clamped in place over a Woulfe's bottle which also acts as a trap for oil coming from the pump. A convenient pressure setting has been found to be 8 lbs/sq. in., and thus the air pressure to the apparatus can be regulated from zero to 8 lbs/sq. in. by means of a suitable valve, e.g. a screw clip.

(2) With all the methods of air supply used above the chief impurities in the air were oil from the pump, as droplets, and dust and moisture. The absorption train used in this apparatu

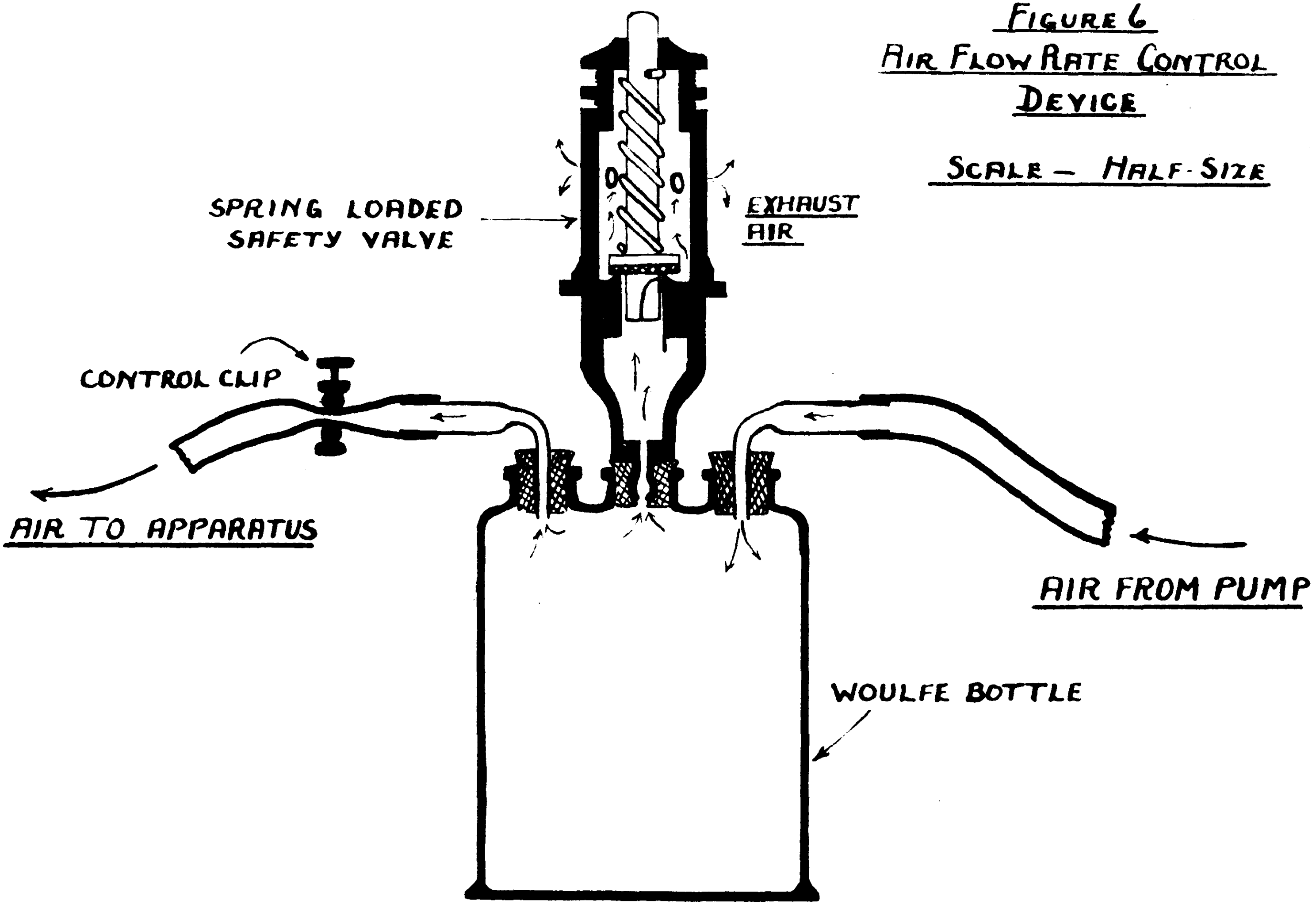


FIGURE 6
AIR FLOW RATE CONTROL DEVICE

SCALE – HALF-SIZE

Wm. Gibb.

consisted of,

(a) A scrubber filled with glass beads and broken glass which could be wetted at intervals with fresh water from the supply vessel (A) and emptied of contaminated water through cock (B).

(b) the trap (C) which caught water spray carried over from the scrubber.

(c) A drying tower (D) filled with calcium chloride and cotton wool for removing water vapour.

(3) The air pressure gauge for measuring pressures on the underside of the sintered disc was a mercury manometer set vertical on a meter stick by plumb line. Pressure difference could be measured by a cathetometer to 0.01 m.m.

(4) In such work where surface tension comes into play contamination is the greatest hazard. This results largely from dust in the atmosphere and traces of grease from hands and mouth. It was therefore decided to prepare the frothing solutions in situ. This was done as follows. Distilled water was supplied to the apparatus by the burette and bottle device generally used to supply stock solutions in the laboratory. This has the advantage that the liquid is always taken from under the surface. The alcohol was supplied through an opening in the other side of the frothing tube from a specially shaped burette as shown in the diagram. The burette stop-cock barrels were held in place by rubber

bands as no grease could be used. It is convenient at this point to mention (6) the frothing tube of the apparatus. This consisted of a 100 cm. length of 30 m.m. glass tubing fitted with opening (E) for alcohol burette, and stop cock (G). A paper cm./mm. scale was fixed on the outside of the tube so that the divisions could be read through the tube from the front. A piece of wide bore rubber tubing connected the lower end of the tube to an inverted crucible fitted with a sintered disc. The above mentioned scale was so arranged that its zero coincided with the upper surface of the sintered disc. To the other end of the crucible by a rubber joint was fitted a further piece of glass tubing with stop-cock (H) and inlet for air supply. This stop-cock facilitated the removal of solutions after use as demanded above by.....(5)

(5) In one position of this cock the underside of the disc was subjected to the vacuum of a water pump which caused the contents of the frothing tube to be sucked into the waste bottle (W). The second position of the cock was used in conjunction with cock (G) to return any solution passing through the disc before it was required to do so to the main body of solution.

A solution of known strength was prepared in the frothing tube as follows.

With a slight pressure of air on the apparatus and cock (H) turned so as to return liquid to the frothing tube, a known volume of water was run from the burette via stop-cock (G) into the tube. A known volume of alcohol was now added through (E) and the opening closed with a rubber stopper. The air pressure was then raised to mix the contents of the tube then lowered to stop the frothing. A further known volume of water was added from the burette to bring it up to an arbitrary level in the frothing tube. The strength of the solution in the tube could now be calculated.

The froth could now be produced by bringing the air pressure on the underside of the sintered disc up to the required level as shown by the manometer, after closing all the above stop-cocks.

Before use, the frothing tube was always thoroughly cleaned with chromic acid followed by distilled water.

It was not long before the rubber joint between frothing tube and sintered disc crucible gave trouble. At high concentrations of ethanol, substances were leached from the rubber which raised the froth stability markedly. The joint was therefore remade using polytheme as a cement.

The surfaces concerned were ground with carborundum power to make intimate contact and then were heated to 250 C. The heated parts were wiped with polythene then clamped firmly together and allowed to cool. The joint gave no further trouble and had not the slightest effect on the froth stability of solutions.

Preliminary Work.

Before starting the main series of tests some preliminary work of a qualitative nature was carried out, and the observations made are in general agreement with previous workers.

Solutions of ethanol in water were found to be very suitable as frothing media, since their frothing power was sufficiently low to keep the column of froth within the apparatus at a convenient value of air pressure. It was found that with an adequate volume (about 75 ccs.) of dilute ethanol solution in the frothing tube, the froth formed at any given air pressure was in a state of dynamic equilibrium such that the froth height was constant for that pressure. This could only happen if the rate of loss of air at the top of the froth by bubbles bursting there was exactly equal to the rate at which the applied pressure caused air to be supplied as bubbles at the base of the froth. This equilibrium height increased with increase of pressure. At lower pressures there was a definite demarcation line between the froth proper and the bubble-containing liquid. As the pressure was increased and the froth height rose this line fell as the liquid was converted into froth. A point was finally reached where the line disappeared and the liquid seemed to have been completely turned into froth.

The average size of bubble increased slowly with increasing pressure then at quite a definite point very large bubbles began to appear in the froth mass, few at first, then many as the pressure was further increased.......until the froth was being agitated and broken up by the large globules formed. The pressure at which the large bubbles first made their appearance was called the Limiting Pressure, and the corresponding height of the froth as the Limiting Froth Height.

For increasing concentration of alcohol the average size of bubble in the froth decreased. This is to be expected from the decreasing surface tension.

A determination was made of the limiting froth height and limiting pressures for various concentrations of alcohol. The solutions were prepared in the apparatus as described above, 75 ccs. being made up in every case. Since the volume of solution taken was constant it was decided to always measure froth heights from the sintered disc as zero line. This was simpler than measuring them above the height of the liquid at rest as it only involved taking the reading of the height given by the cm. scale on the frothing tube. The readings obtained are plotted in Figure 7. The height of the liquid level at rest is given for comparison. It should be noted that these values are purely relative but show the trend of the variables. It can be seen that the limiting values decrease with increasing concentration following a roughly hyperbolic law.

It is considered that the limiting froth height corresponds to a state where the liquid has reached its

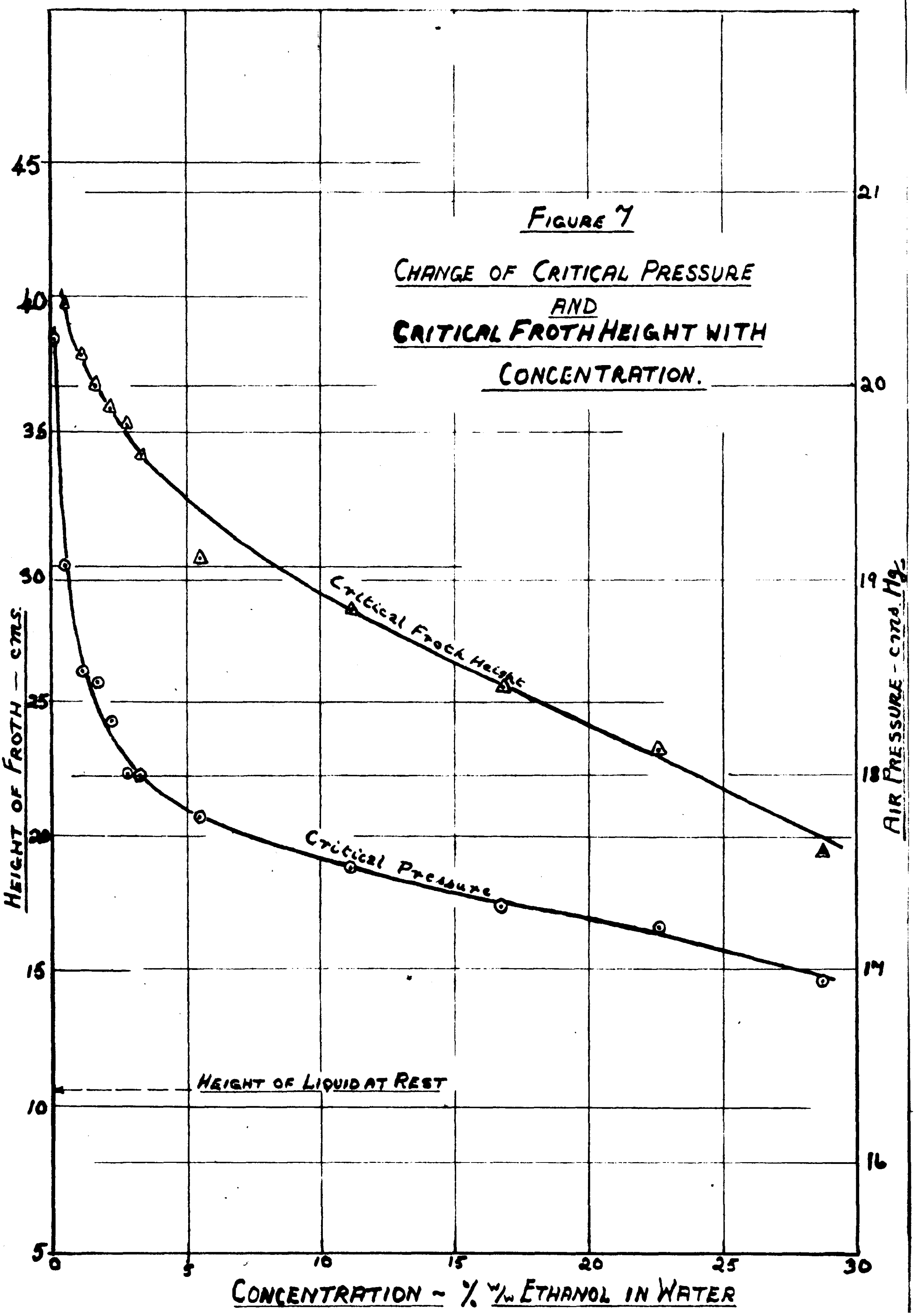


FIGURE 7

CHANGE OF CRITICAL PRESSURE AND CRITICAL FROTH HEIGHT WITH CONCENTRATION.

limit of dispersion and the rate of inflow of air is equal to the rate of return of liquid to the diaphragm to form new bubble films. Above the limiting value there is not enough liquid available at the diaphragm to form normal sized bubbles so numbers of pores group together to form a large bubble with the liquid available. Since the average bubble size decreases with decreasing surface tension, i.e., increasing concentration of the alcohol, the amount of liquid per unit volume of froth increases; thus the limiting value of dispersion is reached at a lower pressure and corresponding froth height. The curves obtained for the plot of pressure and froth height against concentration should be somewhat similar to the plot of surface tension against concentration for the same solutions. As can be seen from Figure 7. this is the case.

From this preliminary survey it appeared that the amount of froth formed under standard conditions would be effected by the following variables,

1. Pressure of inflowing air.
2. Rate of inflow of air.
3. Amount of liquid initially in the tube.
4. Temperature of liquid, air, and surroundings.
5. Surface tension of liquid in tube.
6. Constitution of liquid, i.e. nature of surface active agent and its concentration.

Of these variables the first four are particular to the apparatus and the last two to the frother under consideration. In the portion of work which follows these apparatus variables are studied in detail.

The Variation of Froth Height with Applied Pressure.

Various solutions of aqueous ethanol were used for these tests. Pressures were measured on the manometer in centimetres of mercury by the cathetometer reading to 0.01 mm. 75 ccs. of solution were taken in every case and froth heights were read directly off the scale as before. At most of the pressure values the froth height could be read to the nearest mm., but at high pressures the increased size of the bubble made the error greater. It was soon found that it was difficult to obtain consistent results unless the pressure value in question was approached always in the same way, i.e., always, say, from a lower value. Two slightly different froth heights could be obtained depending on whether the pressure was raised or lowered to the value to be measured. This phenomenon is studied more fully later. For the purposes of the present tests froth heights were always taken on an increasing pressure value. The results obtained were plotted on Figure 8. Curves are given for two typical ethanol solutions and a corresponding curve for the same volume of pure water. This last should not really be called a froth height curve as no froth is formed, but the bubbles passing up through the liquid increase its volume and raise the level to the extent shown. The readings for this curve were difficult to take due to the size of the bubbles.

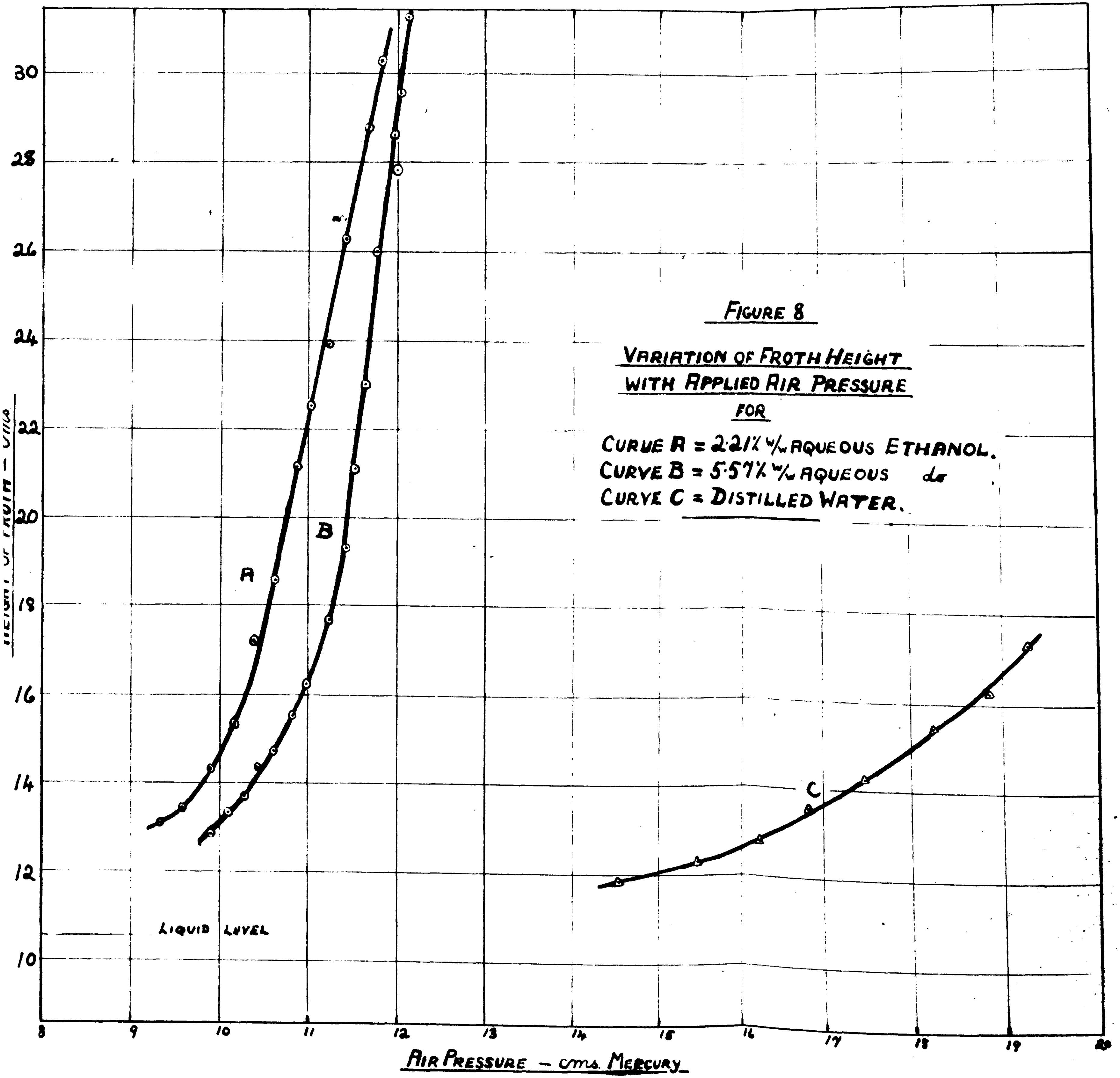


FIGURE 8

VARIATION OF FROTH HEIGHT WITH APPLIED AIR PRESSURE FOR

CURVE A = 2·21% w/w AQUEOUS ETHANOL.
CURVE B = 5·57% w/w AQUEOUS do
CURVE C = DISTILLED WATER.

A test was made to see if evaporation of alcohol occurred during the frothing tests. A solution was frothed at constant pressure for a half hour without significant change in the froth height. Thus evaporation does not appear to take place to any extent from such dilute solutions as are under consideration.

Considering Figure 8, it can be seen that although the graphs for the frothing solutions are initially curved they soon straighten and seem to follow a straight line law,

i.e. $$H = m.P + C \text{ -----------------------} (8)$$

Where H is the height of froth above the bubble origin at the sintered disc, and P is the applied pressure. The gradient m increases with froth stability. The constant C should be the pressure required to start frothing.

Rudolf (42) obtained curves of a similar nature and in discussing their theoretical significance considered that the applied pressure ($P_{\circ}$) was made up of

1. P_1 pressure to overcome pore resistance.
2. P_2 pressure to expand the bubble to equilibrium size at time of detachment against the hydrostatic head of the froth column

i.e. $$P_{\circ} = P_1 + P_2 \text{ -------------------} (9)$$

He took the equation no further.

Rudolf's "applied pressure" is really only the pressure required to start bubbling against the resistance of the apparatus, i.e. pore friction, froth head, etc. It takes no account of that portion of the applied pressure required to maintain the rate of air flow which in turn keeps the froth in dynamic equilibrium, and is therefore considerably less than the applied pressure P in equation No. (8) above. It becomes equal to C when there is no froth in the tube, and is therefore best termed the Resistance Pressure.

By developing Rudolf's Equation (Equation No. (9)) the Resistance Pressure can be determined for any conditions.

P_1 above is further made up of the physical pore friction pressure drop and the pressure required to overcome the surface tension of the solution,

$$\text{i.e.}\quad P_1 = P_3 + \frac{2S}{r}$$

where S is surface tension and r is the pore radius. Thus for any given pore or range of pore sizes with a constant average diameter, P_1 is constant.

Now $P_2 = \rho .\ g .\ h.$

In evaluating P_2, however, the values of ρ. and h will depend on the amount of air dispersed as bubbles at the given moment throughout the froth column.

Let the volume of water in the column $= V$ ccs.

Let the radius of the frothing tube $= R$ cms.

$\therefore$ Equivalent height of water in tube $(h) = \frac{V}{\pi R^2}$ cms.

Let volume of air as bubbles in the column $= V_1$ cms.

$\therefore$ Equivalent height of air in tube $(h_1) = \frac{V_1}{\pi R^2}$ cms.

Let density of water = X gms/cc.

Let density of air in bubbles = X gms/cc.

Now with the top of the froth column at a distance H cms. above the porous diaghragm the hydrostatic pressure on a newly formed bubble is :-

P_2 = Mean density of froth column × g × H

g being the gravitational constant.

The mean density of the froth column is given by $\frac{V.x + V_1 .x_1}{V + V_1}$

$$\therefore \quad P_2 = \frac{(V.x + V_1 .x_1)}{V + V_1} g.H$$

$$= (hx + h_1 x_1)g$$

But $h_1 = H-h$

$$\therefore \quad P_2 = \left[hx + (H-h)x_1\right] \times g$$

The effect of the capillary lift on the column of froth must be taken into account. If the liquid of the froth completely wets the walls of the frothing tube this capillary pressure

$$= - \frac{S.\ 2\pi R}{\pi R^2} = - \frac{2S}{R}$$

Thus the complete expression for the resistance pressure becomes

$$P_0 = P_3 + \frac{2S}{r} + \left[hx + (H-h)x_1\right] g - \frac{2S}{R}$$
$$= \left[P_1 \quad - \frac{2S}{R} + hg\ (x-x_1)\right] + Hgx \text{ ---------------- } (10)$$

Now for a given set of conditions the expression within the squared bracket is constant, say K

$\therefore \underline{P_0 = Hgx_1 + K}$ ------------------------(11)

This linear equation gives the applied pressure required just to start frothing with any given height of froth above the sintered disc. It cannot be determined experimentally in presence of a froth, since if the pressure were dropped to the level required to start bubbling the froth would start to collapse upsetting the initial conditions. It could be calculated, however, by finding the pressure just to start bubbling with various heads of water on the sintered disc and by substituting values for the other constants and variables in the equation.

The difference $P - P_0$ is directly proportional to the height reached by the froth above the point of formation of the bubble. Thus it appears that a froth column in dynamic equilibrium behaves like a jet of water directed vertically upwards from an orifice, in that the height reached is proportional to the applied pressure. The kinetic energy imparted to the gas bubbles is converted into potential energy which is proportional to the pressure causing motion.

This explains the linear portion of the curves but not the initial curved portion. The curved portion suggests that P_1 is not constant in that region; i.e. the radius of curvature of the pores (r) is not constant. This can only be the case if different sizes of pores are coming into play as the pressure is increased. This is just what we would expect, since only the large pores will gas at low pressures and as the pressure is increased smaller pores will continually be coming into play, until finally all the pores are gassing freely. At this point the average radius of the pores is constant and the straight line law is followed, i.e. since P_0 is now linear with respect to H

$$P - P_0 = mH \quad \text{is also linear.}$$

Hysteresis of the Froth Column.

The previous inconsistency of the froth height obtained at constant pressure, depending on whether the value was approached from a lower or higher pressure, was now investigated.

In case this inconsistency might be due to the apparatus itself an improved frothing tube was designed in Pyrex glass. This was an all-glass structure to avoid the use of rubber joints. The new frothing tube is shown in Figure 9. The method of operation is identical with that of the original tube. To differentiate it from the previous and further apparatus it will be called Frothing Apparatus No. 2. The pores of the new sintered glass disc were rather larger than in Frothing Apparatus No. 1. The mercury manometer was therefore replaced by a water manometer to permit the applied pressure to be measured more accurately. An improved scrubber and absorption train were also designed and built. This is drawn in Figure 10. The absorption train now consisted of a vessel containing solid sodium hydroxide, a

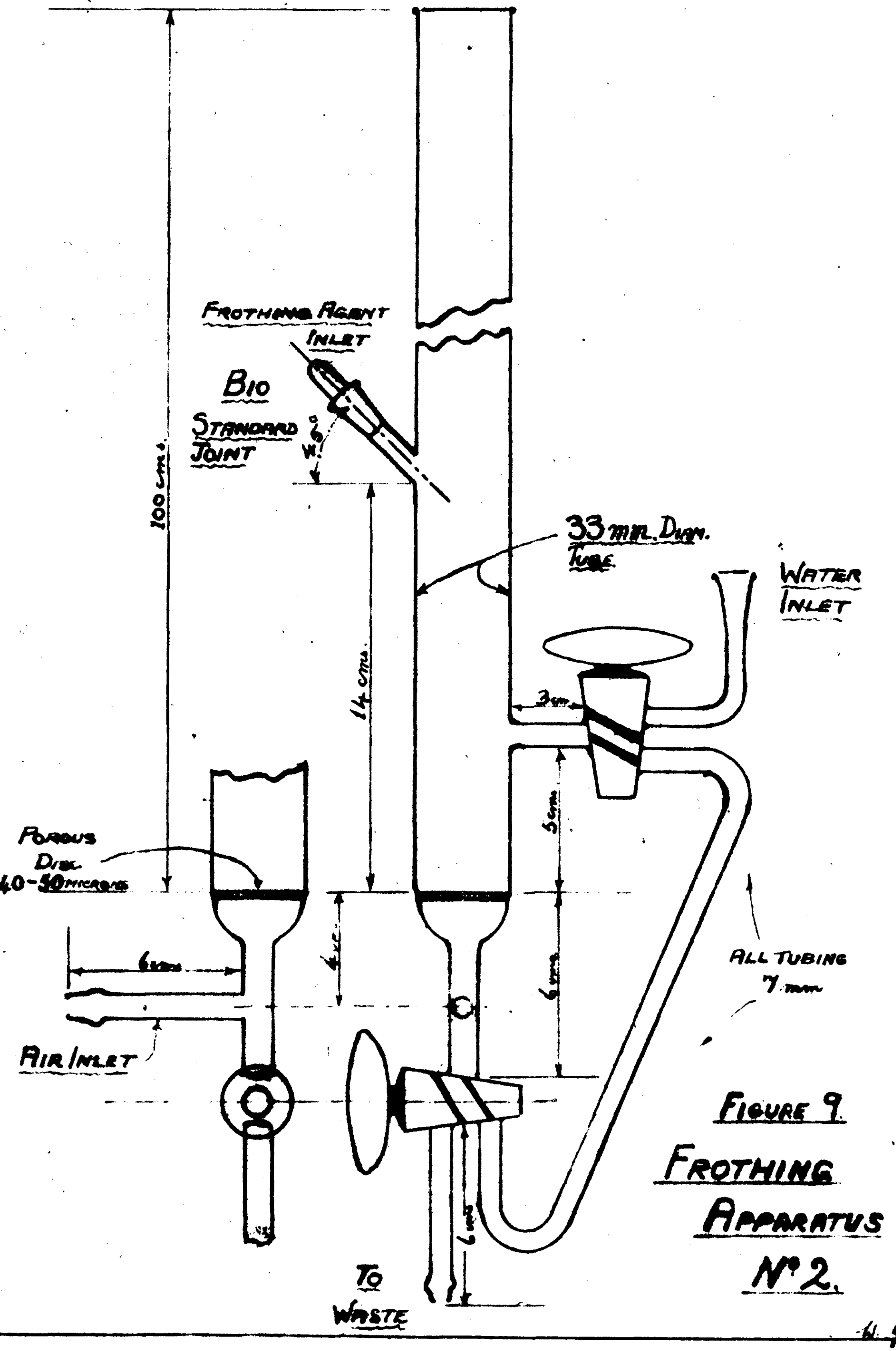


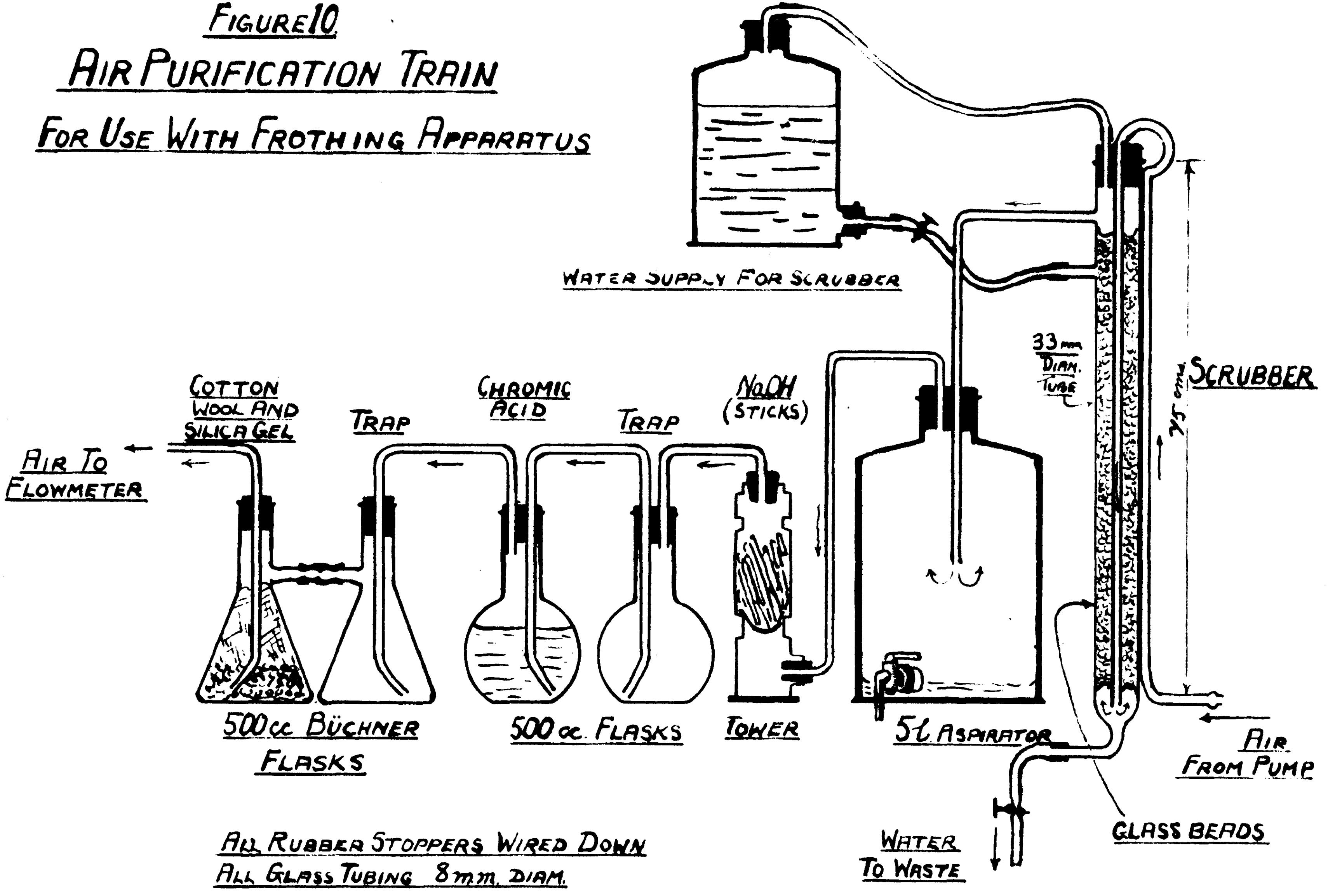
Figure 9

Frothing Apparatus No 2.

Figure 10

Air Purification Train

For Use With Frothing Apparatus



All Rubber Stoppers Wired Down
All Glass Tubing 8 mm. Diam.

W. Gitt

trap, a vessel containing a saturated solution of chromic acid in concentrated sulphuric acid, another trap, and finally a vessel containing silica gel and cotton wool. By this means it was hoped to free the inflowing air of oil, dust and moisture.

It was found that 100 ccs. of solution was a suitable volume for the new tube. The first tests carried out were designed to see if the new apparatus showed the same inconsistency as the old. The solution to be frothed was made up in the usual way from ethanol and distilled water. From now on greater care was taken with the reagents used. The distilled water used was double distilled and condensed on Pyrex glass. The ethanol was the laboratory absolute alcohol redistilled, and its concentration was determined by density measurement. Conc. of redistilled absolute alcohol; 99.4% ethanol.

For the first test in this series a 3% aqueous ethanol solution was prepared in the tube and the pressure of air increased slightly until a small measurable head of froth had formed. The pressure reading was taken and the corresponding froth height noted. The pressure was then increased slightly to a new value and the operation repeated. Care was taken that the pressure never fell in the slightest between readings. The readings were continued for suitable increments of pressure until the maximum dispersion of the solution had been reached. The pressure was then dropped in suitable increments, taking care that the pressure never rose in the slightest between readings, and the readings were continued until the froth was no longer formed. The tube was then rinsed out and the test repeated for a new solution. The results are given for two typical solutions in Figure 11.

The great difference in froth heights for a constant pressure value is obvious from the curves. Evidently this phenomenon was not peculiar to the first frothing tube. The shape of the curve suggests a hysteresis effect, since the froth height obtained on an increasing pressure value is always lower than that obtained on a decreasing pressure value, as if the froth height lagged behind the change in pressure. This was thought at this stage to be due to the incomplete wetting of the glass surface of the frothing tube. As the froth rose over dry non-wetted glass the height reached would probably be modified by the degree of wetting taking place. On the other hand a froth column falling to a definite position would only be moving over fully wetted glass and the final height should be independent of the glass surface. If this theory was correct it was probable that the latter gave a more correct value of the froth height at the applied pressure.

As a test of this theory a series of tests were carried out with the inner surface of the frothing tube deliberately contaminated to make it non-wetting. Various coatings like vaseline, collodion, and wax were tried. The

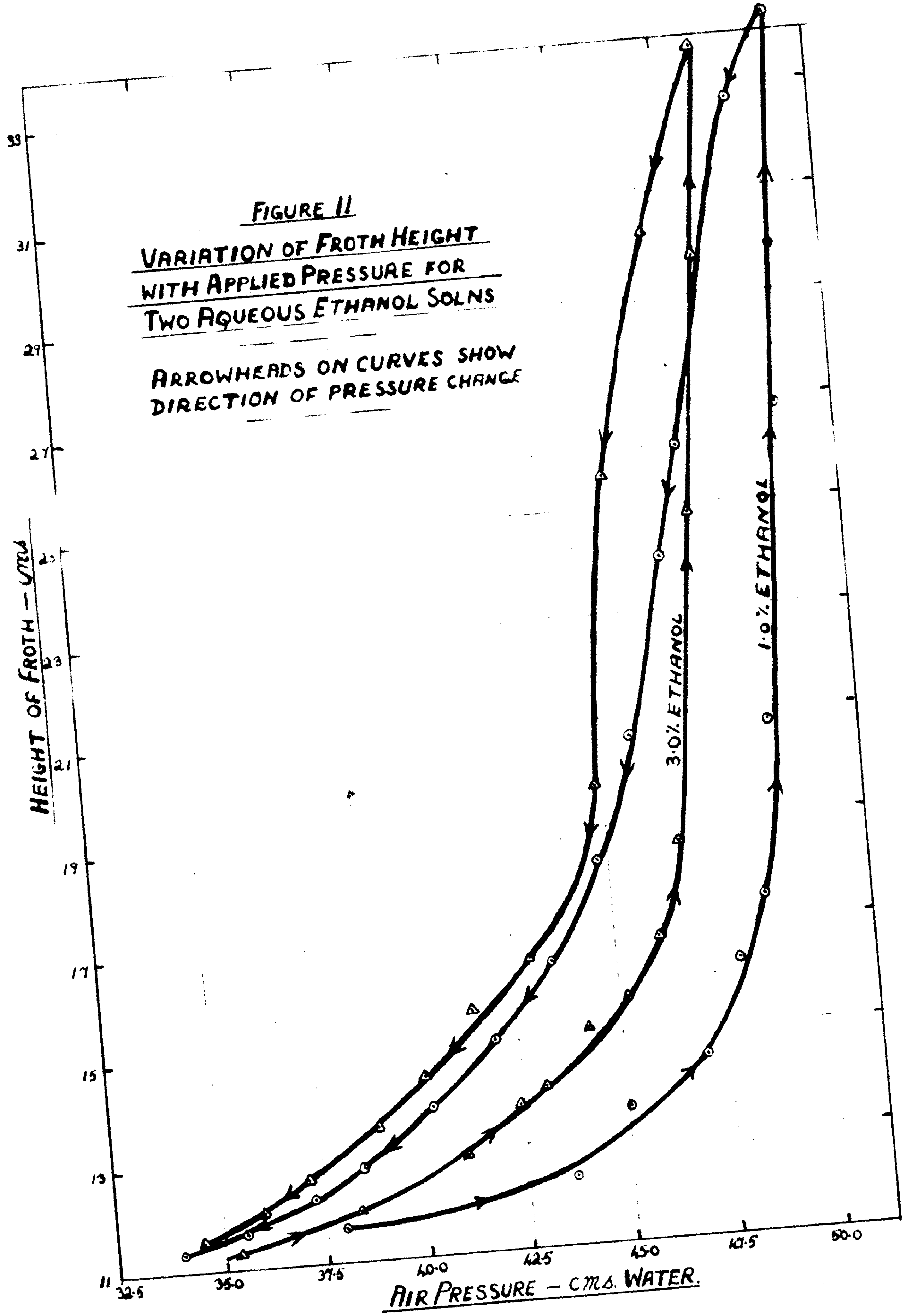


FIGURE II

VARIATION OF FROTH HEIGHT WITH APPLIED PRESSURE FOR TWO AQUEOUS ETHANOL SOLNS

ARROWHEADS ON CURVES SHOW DIRECTION OF PRESSURE CHANGE most durable was produced by rinsing the frothing tube with a very dilute solution of white wax in ether then blowing with air till dry. The ethanol solution was then prepared in the tube in the usual way. A typical result is that shown in Fig. 12. This should be compared with that obtained for a similar solution and a clean tube in Fig. 11. The froth heights for a given pressure are much greater in Figure 12. This was probably due to the dilute ethanol solution extracting the wax from the glass surface. In the case shown in Fig. 12 a series of increasing pressure readings were taken a second time immediately after the froth had been brought to zero the first time. The similarity between the two increasing pressure curves suggests that wetting alone is not the cause of the hysteresis, since it would be difficult to obtain the same degree of wetting on such a surface on two successive runs. On the first run the tube was completely dry, while on the second it was covered with droplets of solution.

The comparison between clean and contaminated tubes is shown better in Figure 12A. In this case a very dilute solution of isoamyl alcohol in water was used, which should have had little solvent action on the wax film. It can be seen that, although the froth stability (as indicated by the froth height at any air pressure) has been affected by the wax, there is little difference between the two in the amount of hysteresis shown.

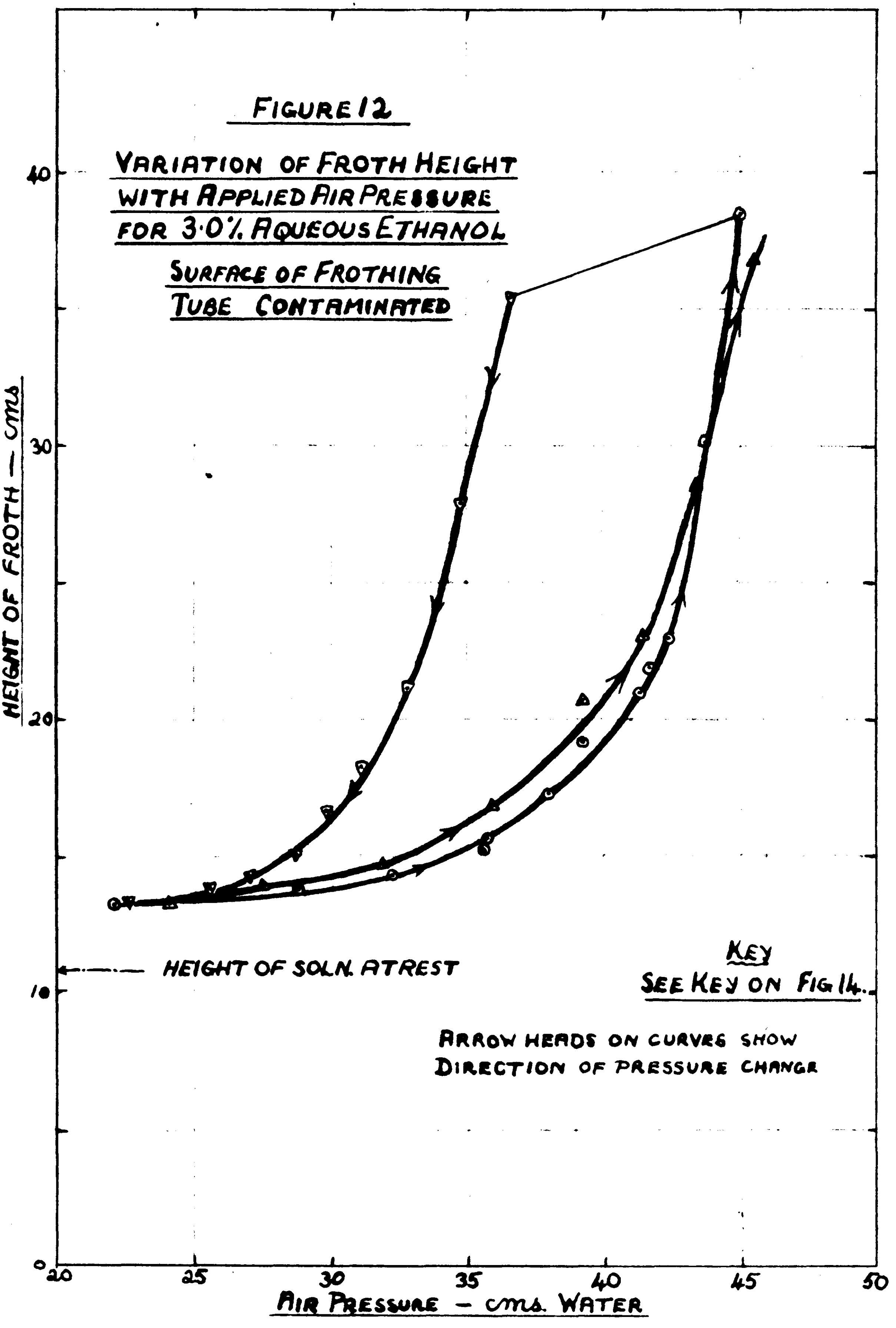


FIGURE 12

VARIATION OF FROTH HEIGHT WITH APPLIED AIR PRESSURE FOR 3·0% AQUEOUS ETHANOL

SURFACE OF FROTHING TUBE CONTAMINATED

KEY

SEE KEY ON FIG 14.

ARROW HEADS ON CURVES SHOW DIRECTION OF PRESSURE CHANGE

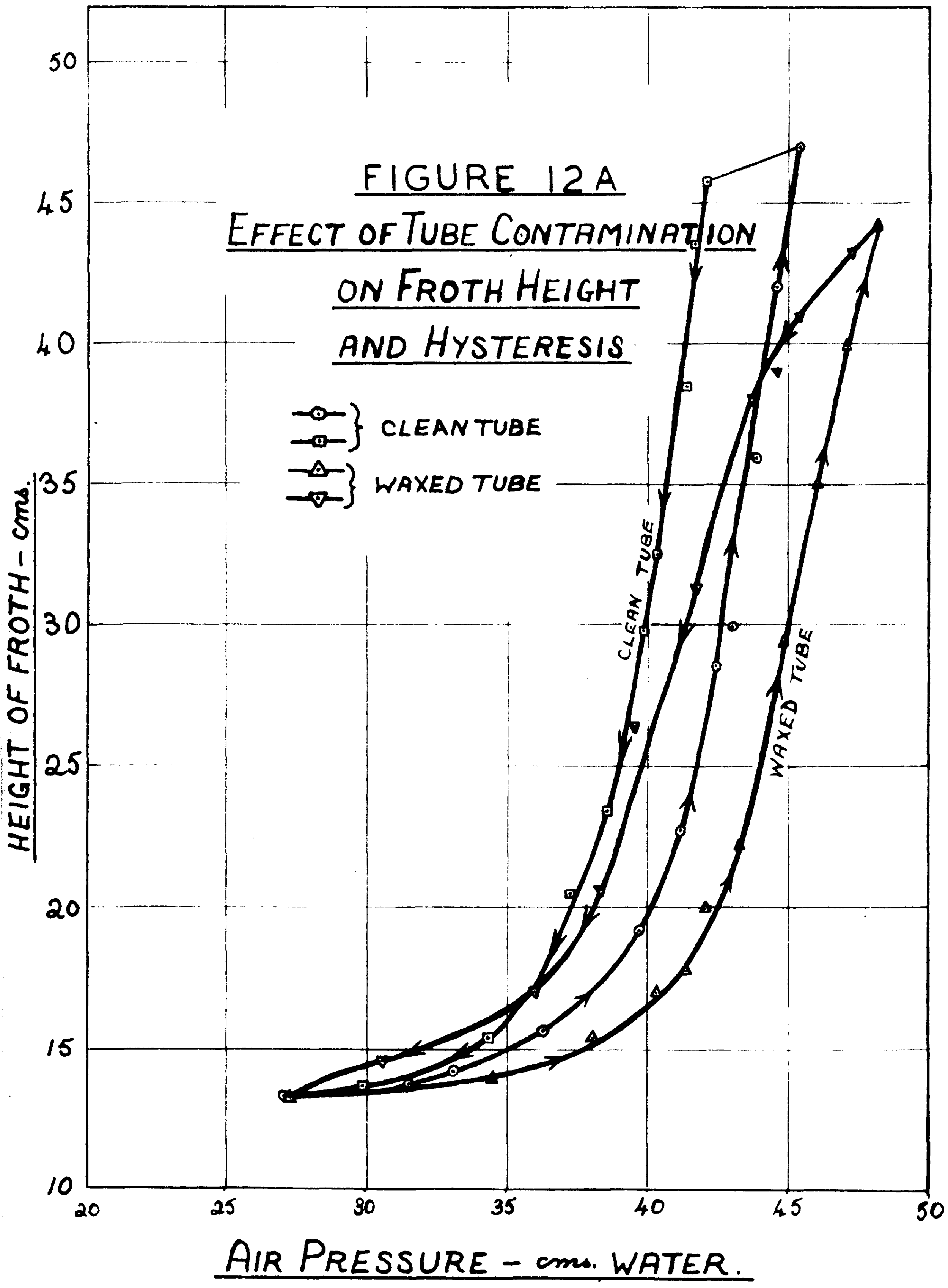


FIGURE 12A
EFFECT OF TUBE CONTAMINATION ON FROTH HEIGHT AND HYSTERESIS

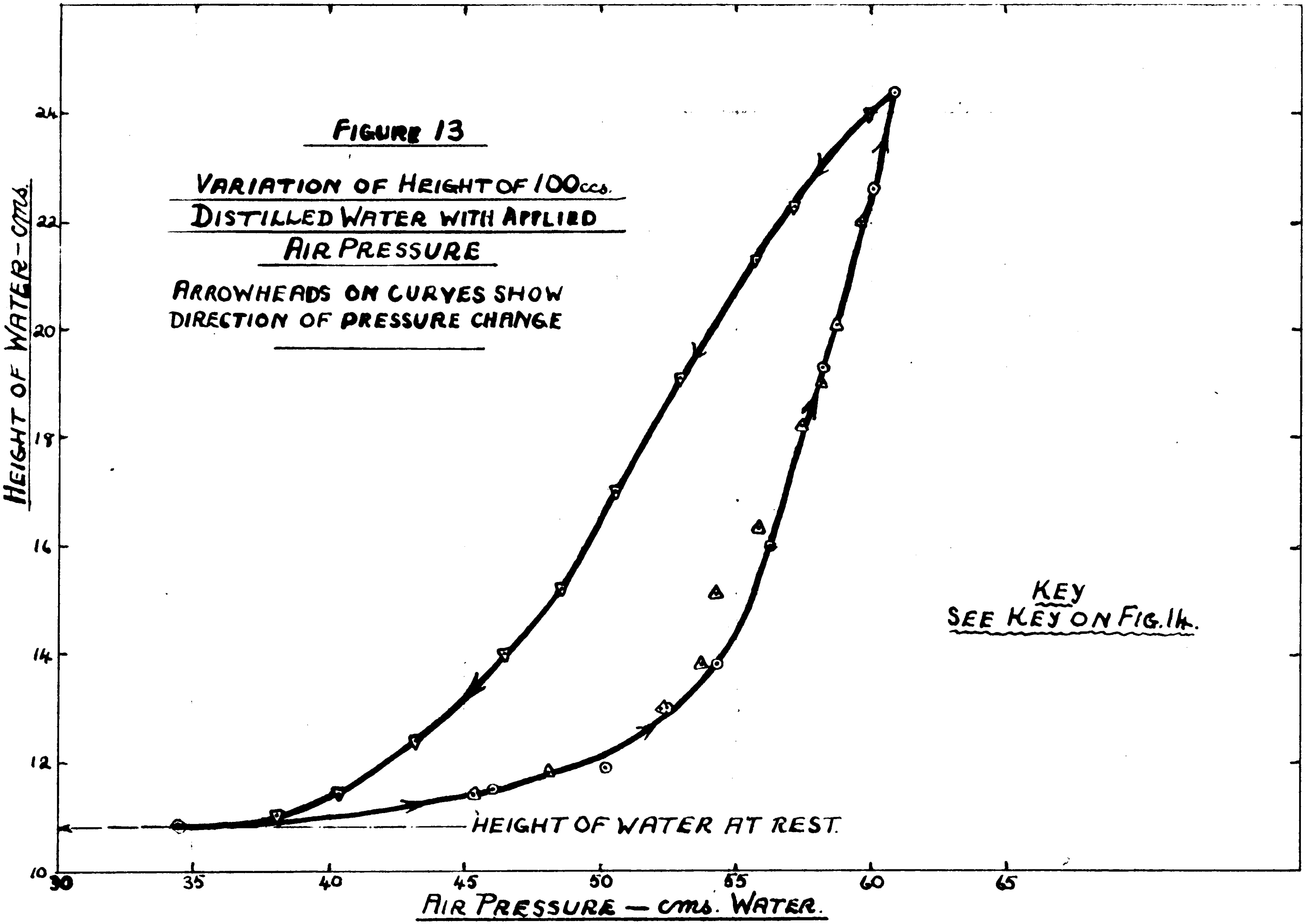


FIGURE 13

VARIATION OF HEIGHT OF 100ccs. DISTILLED WATER WITH APPLIED AIR PRESSURE

ARROWHEADS ON CURVES SHOW DIRECTION OF PRESSURE CHANGE

KEY
SEE KEY ON FIG. 14.

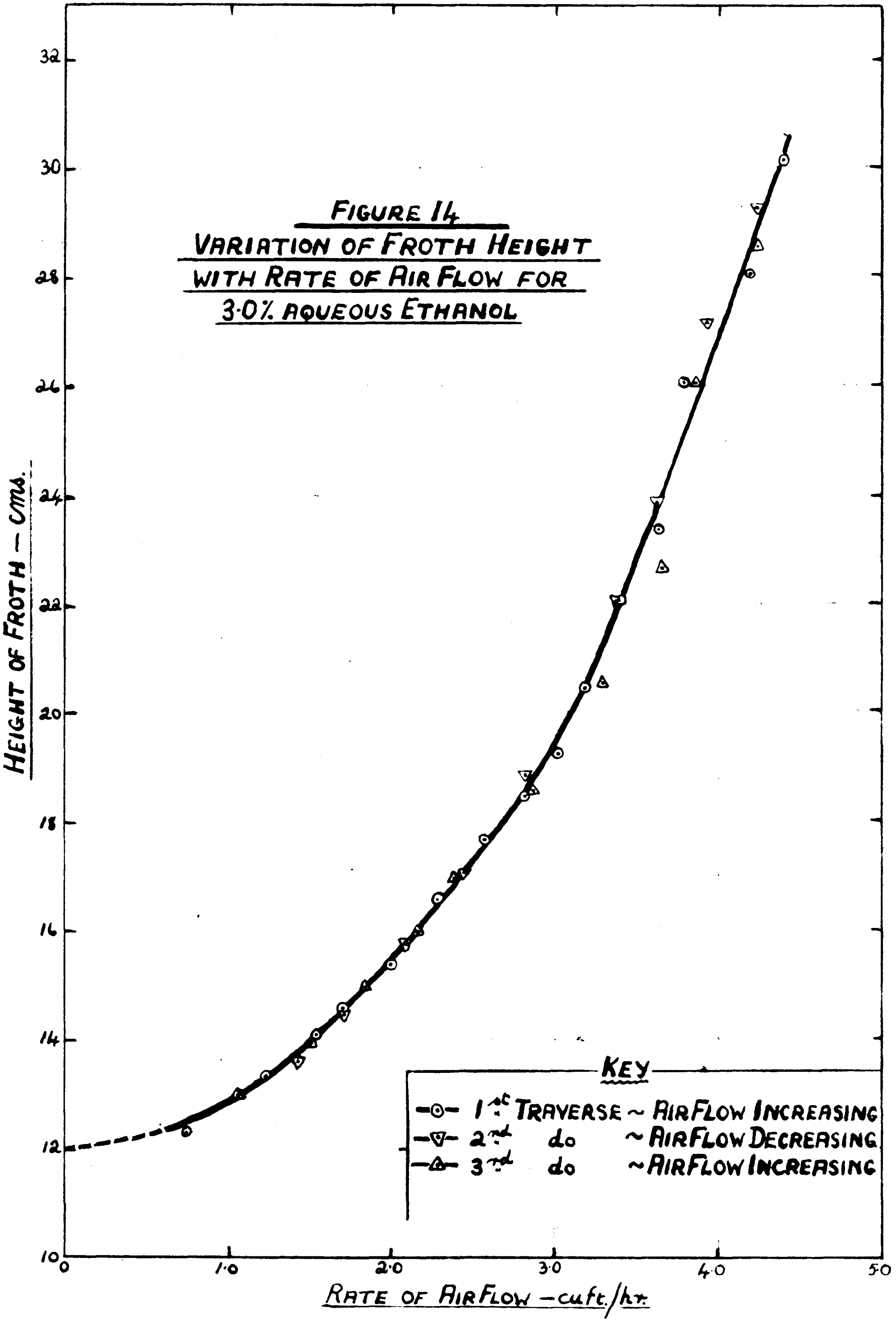
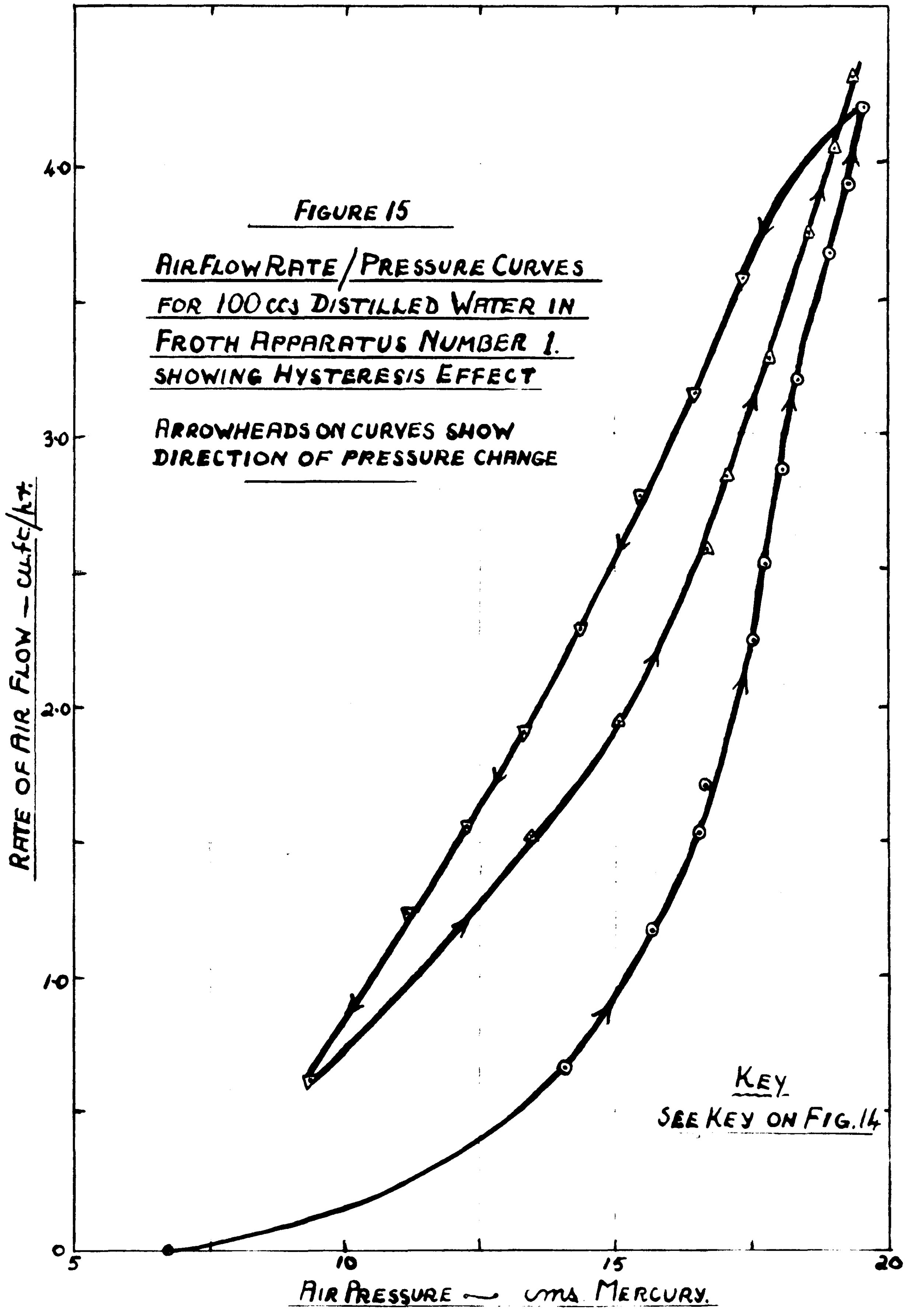


FIGURE 14
VARIATION OF FROTH HEIGHT WITH RATE OF AIR FLOW FOR 3·0% AQUEOUS ETHANOL



hysteresis effect is again evident. It must therefore be due to the changing pore resistance of the sintered disc. This could only occur if the pores are being partially clogged with water. A closer study of figure 15 shows that this must be the case. In the first traverse of the pressure range the pores are badly clogged with water which is gradually blown out as the air flow rate is increased. On the descending traverse the pores have the maximum diameter they reached on the rising pressure traverse, thus the air-flow rate, and the froth height is higher for any given pressure than it was in the previous case. The exact rate of flow value for any second ascending pressure traverse depends on the time the solution is allowed to lie static on top of the pores. If the pressure is increased again immediately, the curve is similarly to that for the descending traverse; if some time is allowed to elapse the pores take up water and "necking" takes place, i.e. the water reduces their effective diamter, and the curve produced is similar to that for the first traverse. Thus the curve is also a function of the time the solution has stood over the pores.

Discussion of Pressure/Froth Height Relationship.

The straight line portion of the height of froth/ pressure curves (Fig. 8.) seemed at first to be useful for characterising frothing solutions, since the gradient of the lines increased with stability. In view, however, of the hysteresis effect discussed above which must necessarily be a feature of all pores diaphragms, the method would be of little reliability. To obtain consistent results very great care would be necessary to ensure a constant degree of "necking" of the pores.

The Variation of Froth Height with Temperature.

A number of tentative experiments had been made on the variation of froth height with concentration of the aqueous alcohol solution and it was found that the curve obtained tended to move with reference to the froth axis, depending on the temperature of the surroundings. A test was therefore made to investigate the effect of temperature on the froth height.

Apparatus (Froth Apparatus No. 3.)

A new apparatus was built as shown in Figure 16. The frothing tube is of much simpler design in this case and is surrounded with a thermostatic jacket. The air for the dispersion is preheated to the same temperature by passing through a coil of copper tubing placed in thermostatic jacket as shown. A loop is made in the air inflow tube below the sintered disc to allow the air to be passed into the tube and the waste solution removed by independent routes. A thermometer indicating the temperature of the water in the jacket passes through this loop. The jacket water is supplied from a thermostatic bath shown in the diagram, circulation being achieved by a small centrifugal pump driven by an electric motor. Since the froth height at constant air flow rate has been shown to be more consistent than that at constant pressure a flowmeter was used to control the air flow. This was of the orifice variety and was previously calibrated by a wet gasmeter. For simplicity the flowmeter was attached

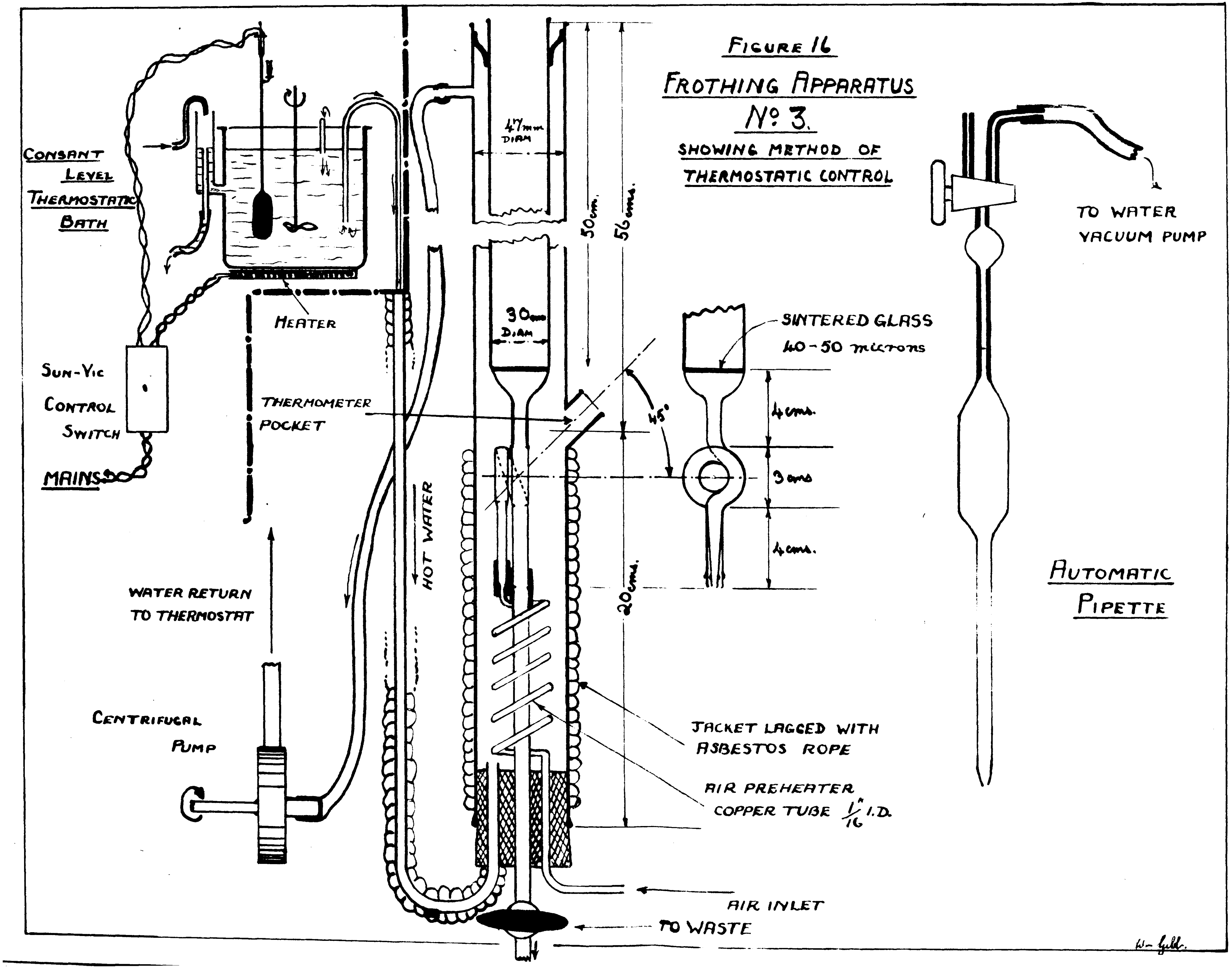


FIGURE 16

FROTHING APPARATUS

No. 3.

SHOWING METHOD OF THERMOSTATIC CONTROL

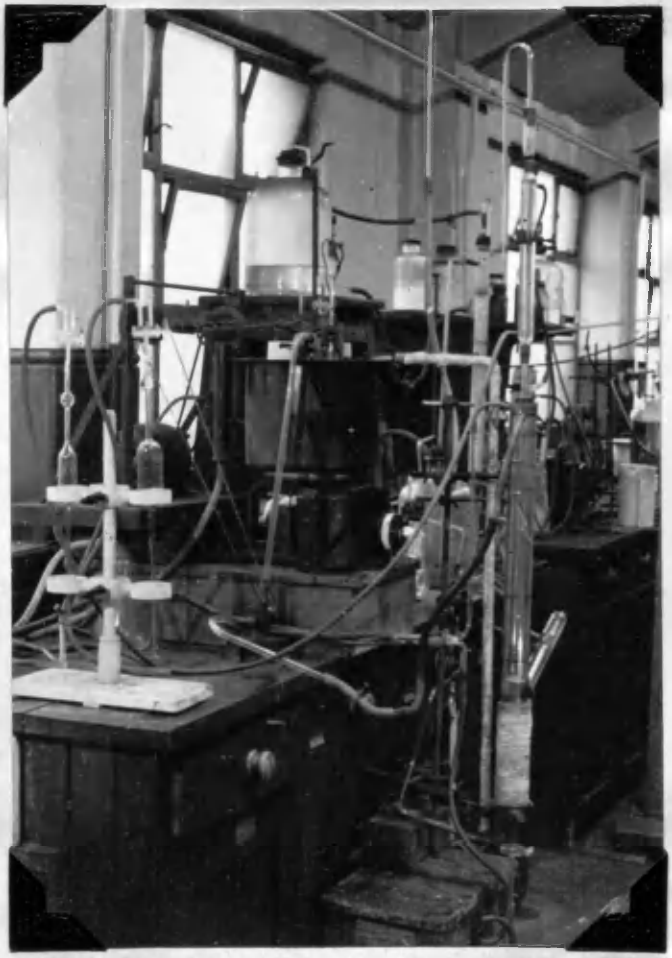


Photo. 2.

Frothing Apparatus No. 3.

Viewed from the side nearest the thermostatic bath; the water circulation pump can be seen, together with two of the automatic pipettes (on the extreme left of the photograph).

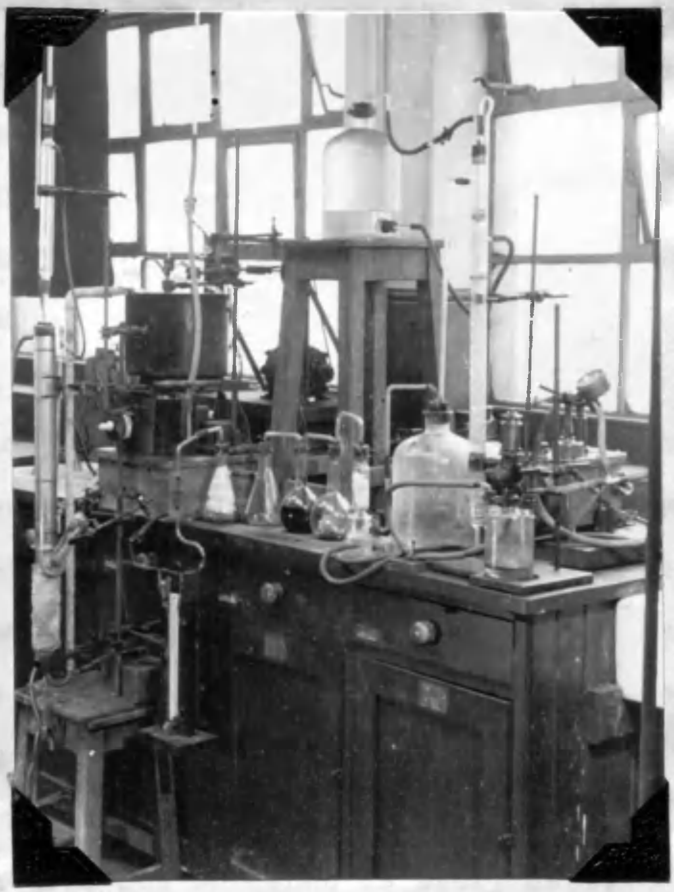


Photo. 3.

Frothing Apparatus No. 3.

Viewed from the side nearest the air purification train. The condenser shown on the top of the frothing tube was designed to prevent evaporation losses but was later found to be unnecessary.

to the air line before it entered the thermostatic jacket. Under the conditions of the experiment a waterproof coating was required to keep the paper scale on the outside of the frothing tube, and therefore, in the water space, from peeling from the tube surface. The most suitable coating was found to be black waterproof enamel covered by two coats of thin shellac varnish. Even this procedure had to be repeated after about four weeks constant use.

Operation.

Since the flowmeter measured the rate of air flow at room temperature, and since it was necessary to have a constant air flow rate through the porous disc for all the various temperatures used, a temperature correction had to be applied to the flowmeter reading to offset the volume change in the air in passing through the preheater. In this way it was ensured that the same volume rate of air flow through the porous disc was obtained in every case.

3% $^{w}/w$ solution of aqueous ethanol was used for all the tests, great care being taken in its preparation to avoid contamination of any kind. With this in view a special automatic pipette was devised for use in transferring solutions from the stock bottle to the frothing tube. It is shown in the same diagram. In one position of the two-way cock the pipette is connected to the vacuum of a water pump, and in the other to atmosphere. Thus the pipette can be filled without using the mouth.

It was decided to measure the froth height at three separate rates of air flow for each temperature tested. The three rates chosen corresponded to readings of 4; 8; and 12 cms. of water, respectively, on the flowmeter manometer. To carry out a test the thermostatic bath was set to supply water at the required temperature as shown by the thermometer passing into the jacket of the frothing tube. At normal temperatures the temperature could be kept steady to within ±0.1°C and at the higher temperatures to within ±0.3°C (at 60°C). When conditions were steady the frothing tube was cleaned out with strong chromic acid followed by distilled water, the liquids being admitted through the top of the tube and drawn to waste through the sintered disc. The loop in the air line prevented the chromic acid from coming in contact with the copper coil. The tube was then rinsed out with the solution to be frothed and 100 ccs. of the solution placed in the tube with a small rate of air flow to prevent the solution passing through the porous disc. A rubber stopper fitted with an inverted U shaped tube was fitted to the top of the frothing tube to keep out dust. A previous test with a thermometer in the frothing tube had shown that the solution took about four minutes to reach the temperature of the jacket, so the solution was frothed gently for five minutes in all cases before taking readings. The flow rate was now lowered to break the froth then raised to the lowest of the flow rates decided upon and the reading of the equilibrium froth height taken.

taken. This was repeated twice more, then the flow increased to the second flow-rate, and finally to the third. The solution was then drawn to waste and the whole operation repeated with a new sample of solution. When the results had been obtained the thermostatic bath was set at a new temperature value. With the apparatus available the highest temperature to be reached was 60°C and by passing the water from the thermostatic bath through a vessel containing ice a number of temperatures below room temperature were obtained.

The results are tabulated in Table I and the curves they give in Fig. 17 for the three flow rates tested. They can be seen to be approximately hyperbolic in shape and show that change of temperature has a greater effect on froth stability at low temperatures than at high. This was important from the point of view of obtaining consistent results and suggested that all future apparatus should be thermostatically jacketed. The curves show that increase in temperature decreases froth stability. This is probably due to the change in surface tension and to the effect of the thermal agitation on the adsorption of the surface active molecules on the bubble film.

Table I.

Variation of Froth Height with Temperature for 3% w/w Aqueous Ethanol.

Room Temp. °C.	Froth Temp. °C.	Corrected Flowmeter Reading Cm.	Equivalent Flowmeter Reading Cm.	Froth Height Readings Cm.	Mean Froth Height Cm.
17	5.0	8.5	8.0	out of apparatus	-
		4.3	4.0	31.0; 30.0; 30.6	30.5
17	10.0	8.3	8.0	43.9; 44.3; 43.4	43.9
		4.1	4.0	24.4; 24.3; 24.2	24.3
19	15.0	12.2	12.0	out of apparatus	-
		8.1	8.0	37.5; 38.0; 37.8	37.8
		4.1	4.0	22.0; 22.2; 22.0	22.1
20	20.0	12.0	12.0	45.8; 46.4; 45.8	46.0
		8.0	8.0	35.4; 35.5; 35.2	35.4
		4.0	4.0	19.2; 21.0; 20.4	20.2
20	25.0	11.5	12.0	39.0; 41.0; 40.7	40.2
		7.8	8.0	30.3; 30.9; 31.3	30.8
		3.8	4.0	18.7; 19.2; 19.4	19.1
20	30.0	11.2	12.0	35.8; 35.5; 35.7	35.7
		7.6	8.0	27.3; 27.0; 27.5	27.3
		3.8	4.0	18.8; 18.8; 18.8	18.8
18	35.0	10.9	12.0	31.7; 32.0; 32.4	32.0
		7.0	8.0	25.6; 25.2; 25.7	25.5
		3.6	4.0	18.4; 18.0; 18.6	18.3
20	40.0	10.6	12.0	29.0; 29.6; 29.7	29.4
		7.1	8.0	24.5; 24.5; 24.0	24.3
		3.5	4.0	18.2; 18.6; 18.5	18.4
25	50.0	10.2	12.0	27.3; 27.2; 27.3	27.3
		7.1	8.0	23.3; 23.3; 23.4	23.3
		3.4	4.0	18.3; 18.3; 18.4	18.3
30	60.0	10.2	12.0	27.4; 26.6; 27.6	27.2
		6.8	8.0	22.5; 22.4; 22.6	22.5
		3.3	4.0	17.7; 18.0; 17.9	17.9

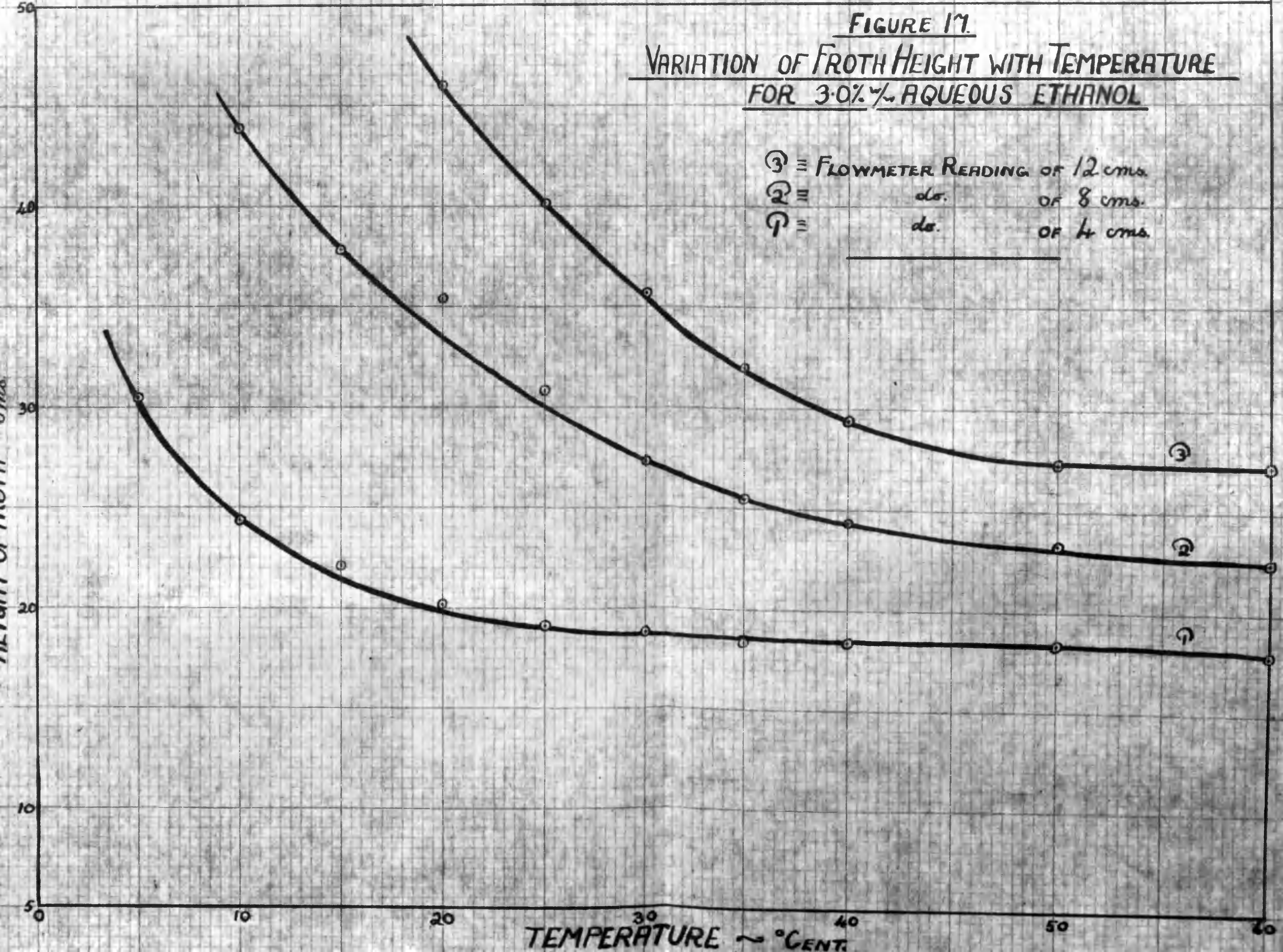


FIGURE 17.

VARIATION OF FROTH HEIGHT WITH TEMPERATURE FOR 3·0% v/v AQUEOUS ETHANOL

Variation of Froth Height and Froth Volume with Rate of Flow of Air.

Bikerman (41) attempted to find "a unit of foaminess" which would be a physical property of the liquid under test and independent of the apparatus, and the amount of material used. He employed an apparatus of the type used by Foulk (39)....a simple bubble column. The pressure for forcing the air through the disc was produced by displacement of water or mercury. The time for a measured volume of air to pass through the apparatus was taken together with the maximum height of froth produced in the tube by the air flow.

He found, (a) The froth volume was a more precise measurement than the froth height, since the latter was a function of the shape of the tube, the froth volume being defined as the difference between the total volume of liquid and froth at the given rate of air flow, and the volume of liquid at rest.

(b) The froth volume was directly proportional to the rate of streaming of the air. Thus if v = volume of froth, V = volume of air forced through the sintered disc per second, i.e. is the rate of flow of air,

Then $v = \Sigma V$ $\quad\Sigma$ being a constant

$$\therefore \Sigma = \frac{v}{V}$$

(c) The value of Σ was independent of air pressure, porosity of sintered disc, and the size of disc.

(d) The value of Σ was independent of the amount of liquid for large amounts of liquid.
Σ had the dimension of seconds, and was the lifetime of a bubble in the froth.

If u is the linear velocity of the air in the froth and h is the height of the froth layer, $\Sigma = h/u$

While if Q is the cross-section of the tube,

$$u = \frac{V}{Q}, \text{ but } h = v/Q$$

$$\therefore \quad h/u = v/V = \Sigma$$

Apart from Bikerman's rather unfortunate choice of the symbol (Σ) for his constant, his "unit of foaminess" is very attractive as it would allow us to assign a definite numerical value to the frothing power of a given frother in flotation practice. This value would then only be dependent on temperature and concentration of frother used in the solution. A critical study was therefore made of this work.

Taking his findings one by one ....

(a) If a uniform tube is used to contain the froth volume (v) it may conveniently be replaced by froth height (h') when comparative values only are being sought. h' is then defined as the difference between the height of froth plus bubble containing liquid (H), previously called in this work "height of froth", and the height of the liquid at rest (h_1)

i.e. $h' = H - h_1$

(b) It should be noted that it is not strictly true that Σ is the lifetime of a bubble in the froth. The error arises in the definition of froth volume (v), i.e. froth height (h'), and Fig. 18 shows diagrammatically how this occurs. The volume of liquid that the bubble has to pass through to reach the froth is not now equivalent to h_1, since the volume has been (1) increased by the volume of the bubbles passing through it, and (2) decreased due to the amount of liquid taken up to form the bubble films. The ideal measurement to make is h_0 (see Fig. 18).....in practice very difficult.

Any variation in Σ will be detected by studying the gradient of the plot of the height of froth (H) or (h') against the rate of air flow (V). A straight line law would prove Σ constant and its value could be easily computed.

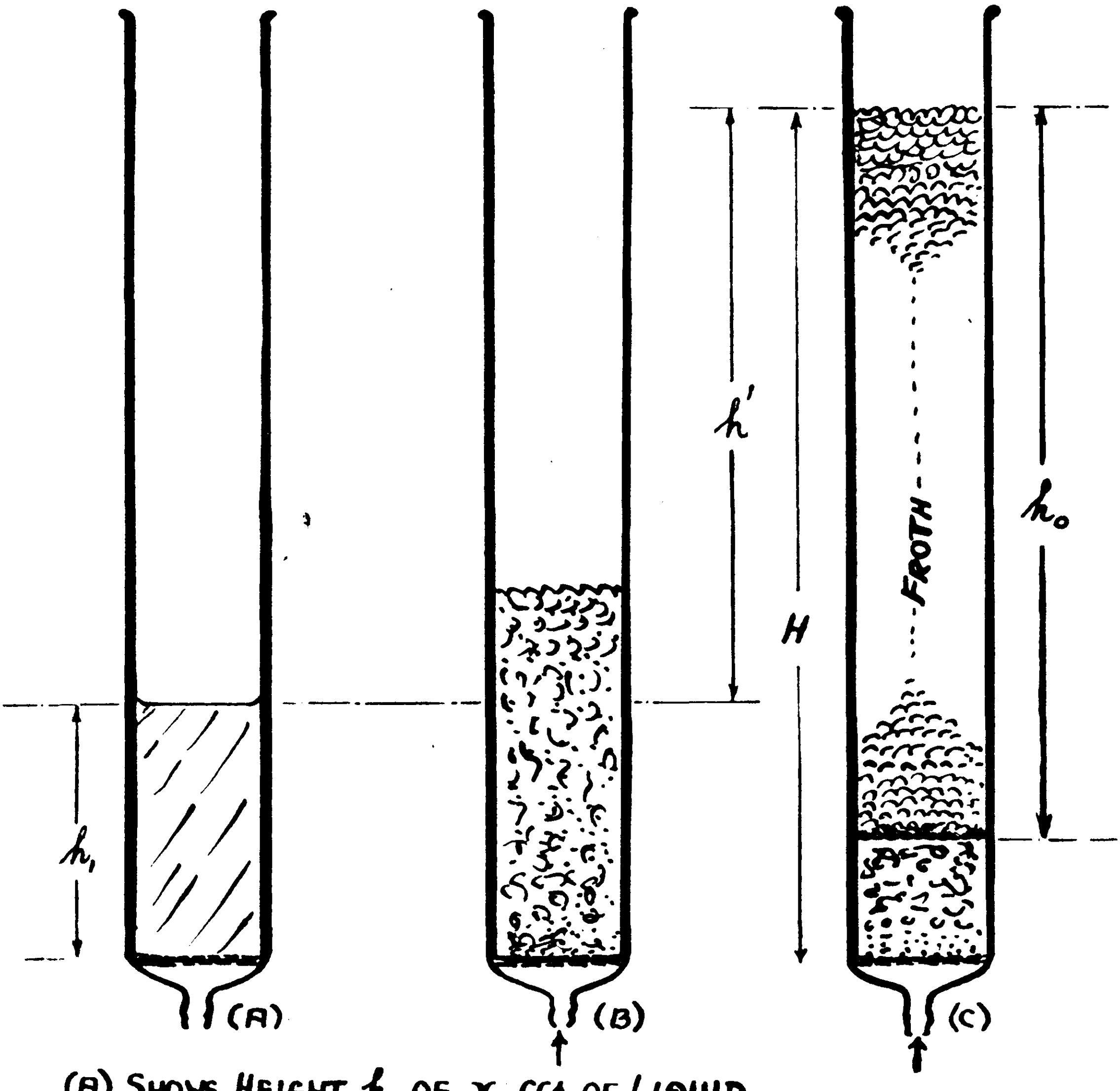
Figure 14 prepared during the work on the hysteresis of the froth column indicates that the relationship between height of froth and rate of air flow is not exactly linear. It appears rather to take the form

$$H = k'V^n + h_1^{\circ} \text{ ------------------------------------ } (12)$$

In this equation (h_1°) has replaced the initial height of the liquid at rest (h_1) since it appears that the curve of Figure 14 does not cut the zero flow rate value at (h_1) but at a slightly higher value. For example 100 ccs. liquid in Frothing Apparatus No. 2 reached a height of 10.6 cms., while Figure 14 gives a value for zero rate of air flow of 12.0 cms. This increase is thought to be due to the volume of liquid contained in the pores of the sintered disc and to the volume of bubbles passing through the solution at an infinitely

FIGURE 18.

ERRORS IN MEASUREMENT OF FROTH HEIGHT



(A) SHOWS HEIGHT h_1 OF x CCS. OF LIQUID.
(B) SHOWS CHANGE OF HEIGHT OF x ccs. OF WATER (NO FROTH) ON BLOWING AIR THROUGH IT.
(C) SHOWS CHANGE OF HEIGHT OF x ccs. OF LIQUID (WITH FROTHING) ON BLOWING AIR THROUGH IT. NOTE THAT LENGTH OF COLUMN OF FROTH IS NOT $h' = H - h_1$, BUT $= h_0$.

small air flow rate. This increased height has been given the term, Virtual Height of the initial solution volume.

The equation,

$$h' = k' V^{n} \text{---------------------------} (13)$$

should also hold, where (h') is now given by

$$h' \quad H - h^{\circ}_{,}$$

and the coefficient (k') and index (n) are constant.

Thus

$$\log h' = n \log V + \log k'$$

and the relationship between $\log h'$ and $\log V$ should be linear.

In Figure 19 the results of Figure 14 are plotted in this form and they can be seen to follow a straight line. The values of the constants for this particular case were calculated to be

$$k' = 0.0138 \quad \text{and} \quad n = 2.00$$

It is suggested here that this value of (n) is universal for solutions frothed in a bubble column.

Thus equation No. 12 becomes

$$H = 0.0138 V^{2} + 12.0$$

and equation No. 13 becomes

$$h' = 0.0138 V^{2}$$

The present apparatus (No. 3.) was quite suitable for measuring heights of froth at varying rates of air flow. Due to recent refinements in measurement of froth height, and to better control of the air flow rate at high rates of flow a more accurate picture of the variation was obtained for

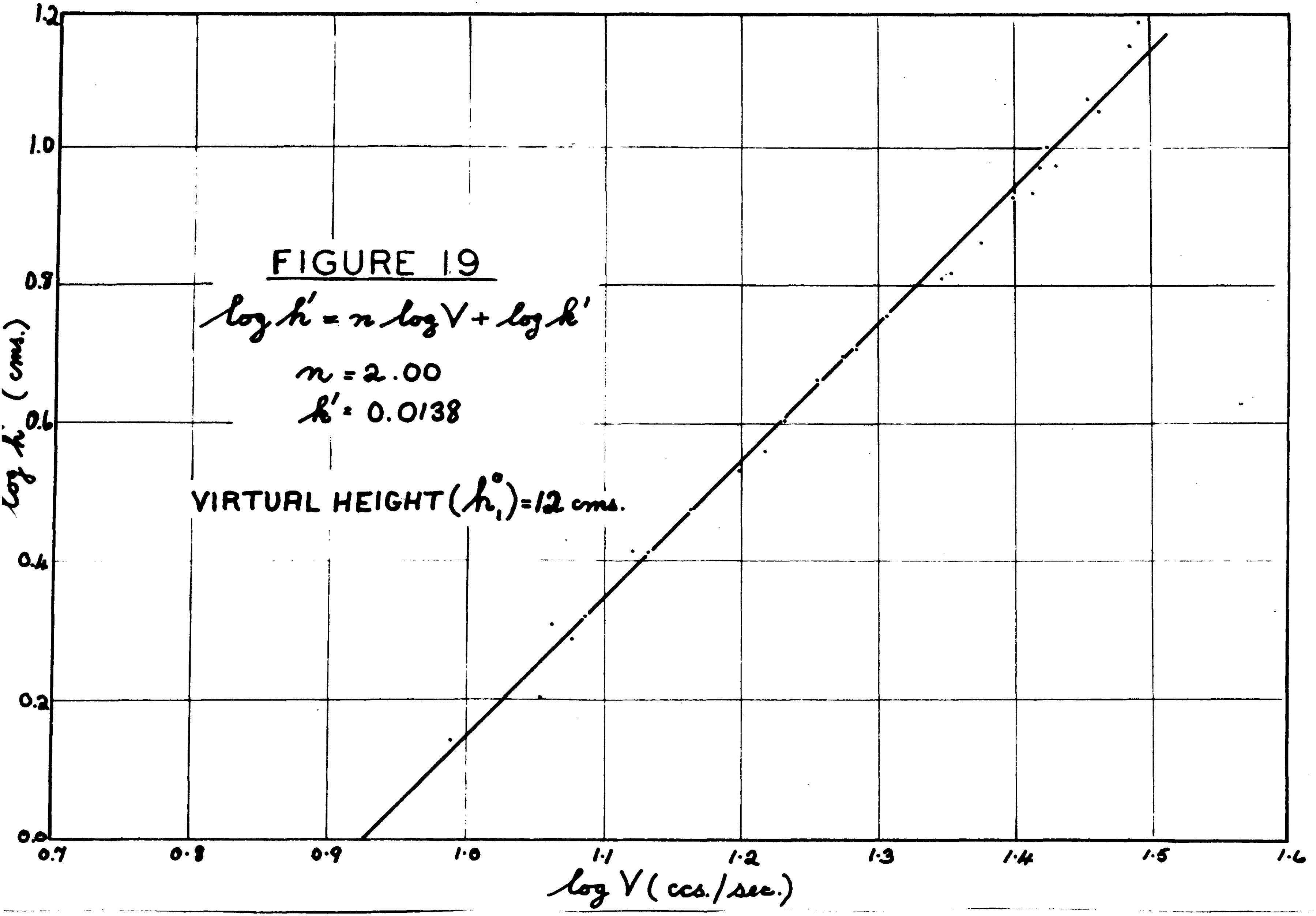


FIGURE 19

$\log h' = n \log V + \log k'$

$n = 2.00$

$k' = 0.0138$

VIRTUAL HEIGHT (h_1°) = 12 cms.

certain isopropanol solutions. 100 ccs. of the solution were frothed in each case. The results are shown in Figure 20. The curves can be seen to consist of a curved portion and a straight portion.

A Larger Frothing Tube (Frothing Apparatus No. 4.).

The present frothing tube limited the froth height measurements to 50 cms. In order, therefore, to increase our range a larger frothing tube was built. The new tube was made to have a reading length of 100 cms. and topped by a B.19 standard ground-glass joint so that a condenser could be fitted if it were required to froth very volatile liquids. In other respects the tube was identical with No. 3 frothing apparatus. A drawing is given in Fig. 21.

Experimental.

Height of froth/rate of air flow curves were plotted for various volumes of solutions of anumber of alcohols (e.g. iso-propanol and iso-butanol) of which the results shown in Fig. 22 for 4.0% iso-butanol solution in No. 4 apparatus are typical. The change from the curved portion to the straight portion which forms a point of inflexion, occurring in this case at an air flow rate of about 1.6 cu. ft./hr., is evident in all the curves.

A New Frothing Apparatus (Frothing Apparatus No. 5.)

The need was felt for a smaller all-glass apparatus for more exact work on these two-phase froths. Such an apparatus should only require about 20 ccs. of solution per

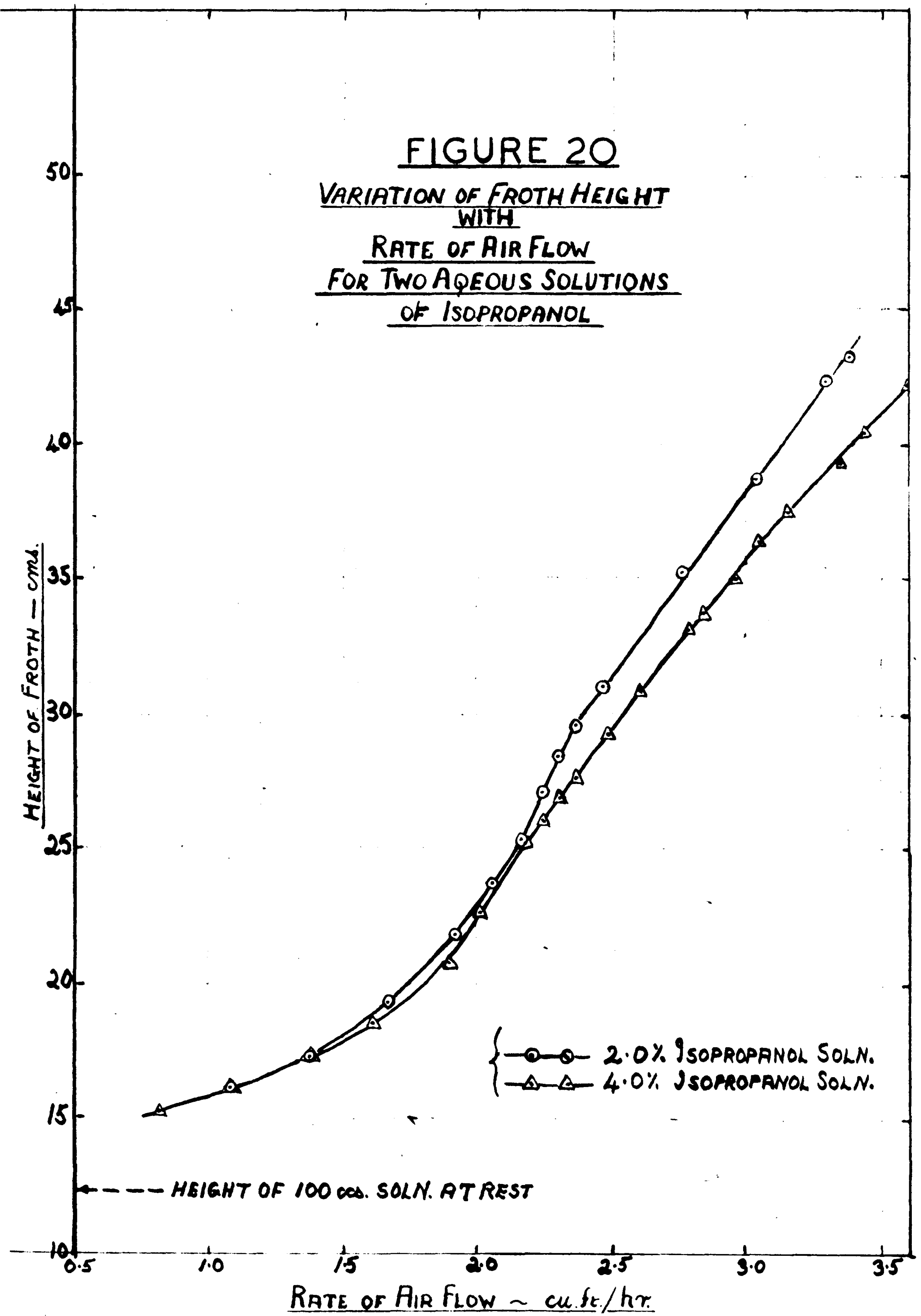


FIGURE 20

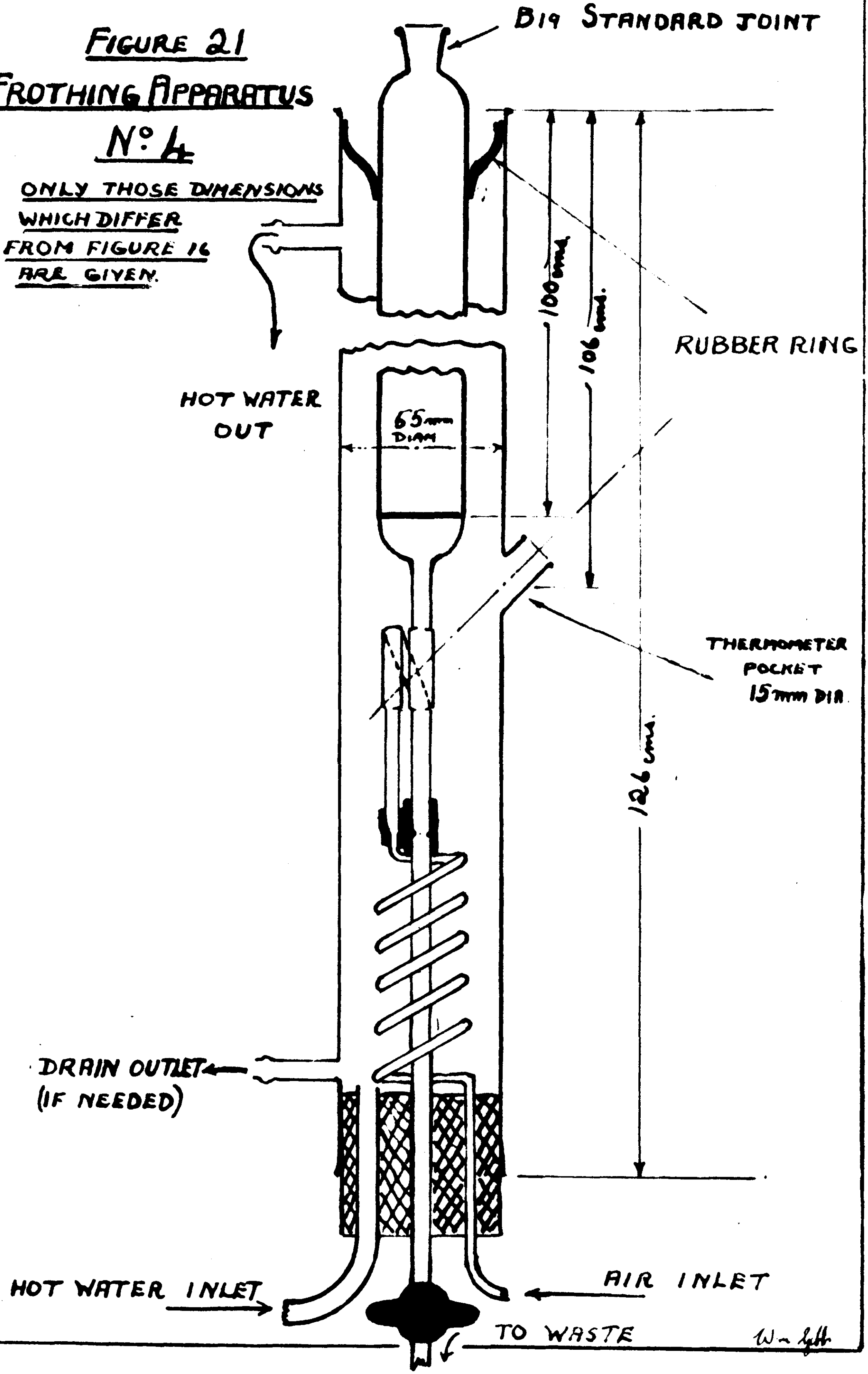
VARIATION OF FROTH HEIGHT
WITH
RATE OF AIR FLOW
FOR TWO AQEOUS SOLUTIONS
OF ISOPROPANOL

FIGURE 21

FROTHING APPARATUS

No. 4

ONLY THOSE DIMENSIONS WHICH DIFFER FROM FIGURE 16 ARE GIVEN.



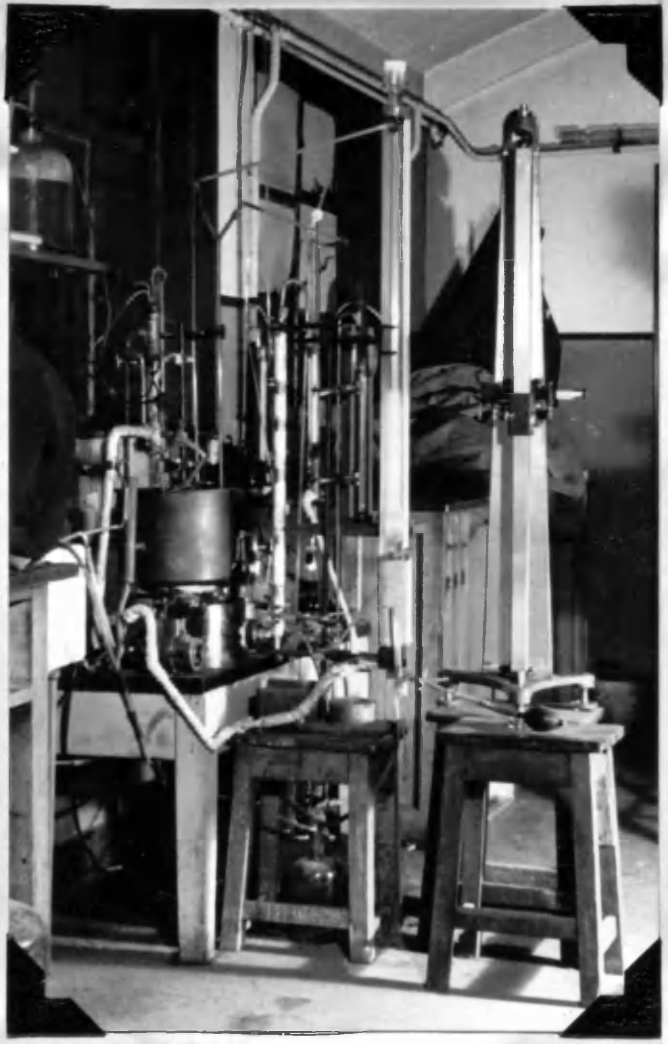


Photo. 4.

Frothing Apparatus No. 4.

The cathetometer used for accurate measurement of froth heights stands to the right of the frothing tube.

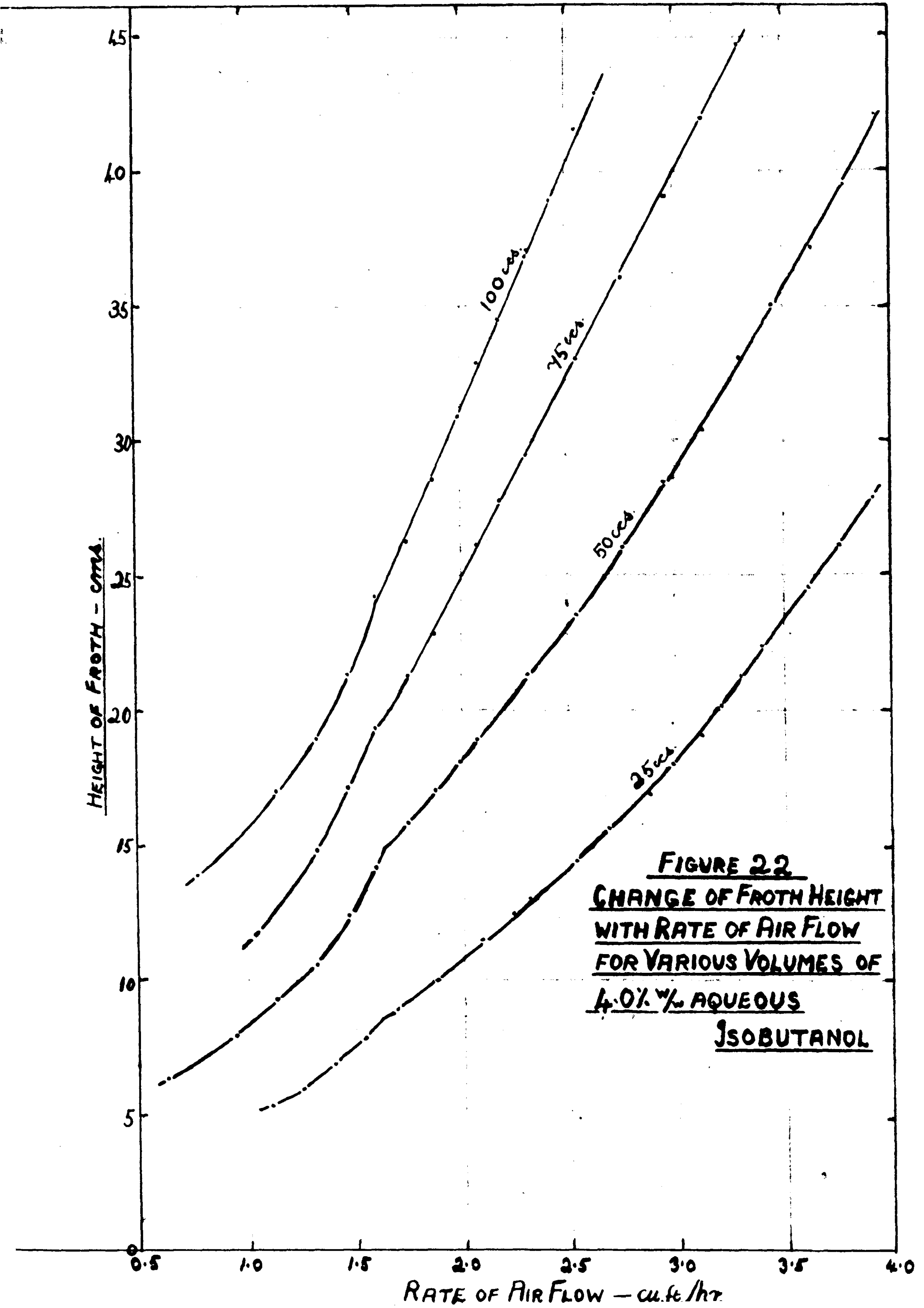
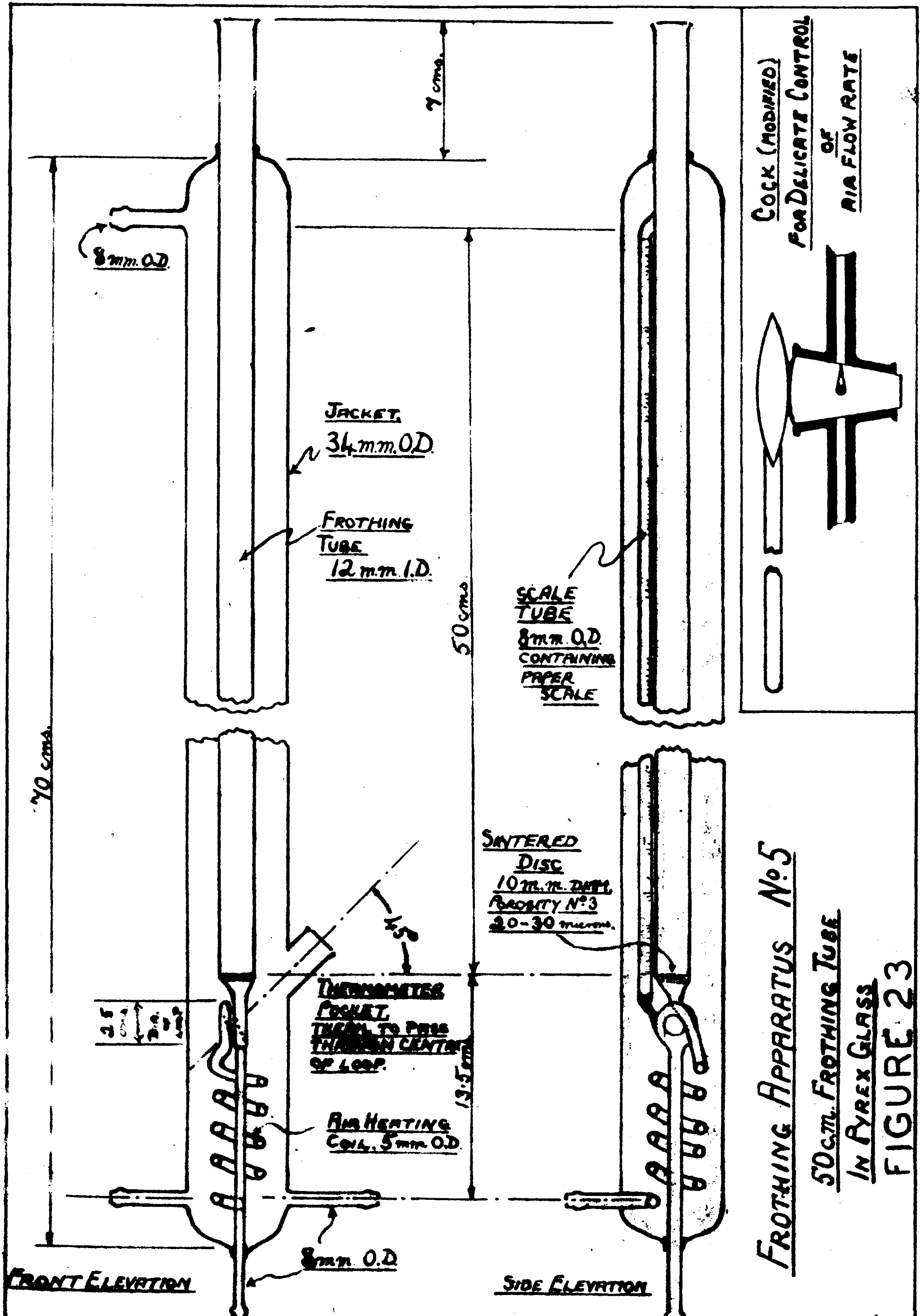


FIGURE 22

CHANGE OF FROTH HEIGHT WITH RATE OF AIR FLOW FOR VARIOUS VOLUMES OF 4.0% w/w AQUEOUS ISOBUTANOL test, and with a much narrower frothing tube and a sintered disc of finer porosity, it would give the frothing characteristics more accurately.

Such an apparatus was designed and constructed. A dimension sketch of it is given (Fig. 23). The apparatus is made in one piece from Pyrex glass. Like previous apparatus it was thermostatically jacketed and had an air preheating coil. The difficulty of the paper scale was obviated by sealing it inside a separate glass tube which was sealed to the back of the frothing tube in the water jacket space, so that the zero of the scale coincided with the top of the sintered disc. The latter had a known porosity (Pyrex No. 3), 20-30 microns. Under operating conditions the temperature of the water in the jacket could be kept constant to within ±0.2°C, the same method of circulation being used as before. The same type of absorption train was used as in the previous apparatus. The control cocks for regulation of the air flow on No. 4 and previous apparatus had been screw clips fixed to the bench and proved quite serviceable. With No. 5, however, the rate of flow of air was required to be so small that screw clips could not give a fine enough adjustment, e.g. maximum air flow rate for No. 5 is about 0.5 cu.ft./hr. The screw-clips were thus replaced with glass stop-cocks with notched keys and extension handles as used for delicate control of gas flow rate in Micro-Analysis



FROTHING APPARATUS No 5

50 c.m. FROTHING TUBE IN PYREX GLASS

FIGURE 23

W. Gill

A drawing is given in the inset to Fig. 23. These proved very delicate in operation and gave very stable air-flow values. The calibration of the flowmeter at such a low flow rate proved a difficulty. It was finally accomplished by weighing the volume of water displaced by the air at atmospheric pressure in a noted interval of time.

Experimental.

Rate of air-flow/height of froth curves were plotted for a number of different alcohol solutions in No. 5 apparatus. Attention was particularly paid to the changing shape of the curves for different volumes of the same solutions, i.e. 5ccs.; 10 ccs.; 15 ccs.; 20ccs.; and 25 ccs. were tested in turn. The temperature of all solutions during frothing was 25 ± 0.2°C. Typical results are plotted in Figs. 24, 25, and 26.

Theoretical.

From a study of the curves we may come to the following conclusions:-

(1) All the curves show a discontinuity.

Note:- This term has been given to the point of inflexion since the law, which the height of froth follows, is discontinuous at this point.

(2) The position of this discontinuity with reference to the rate of air-flow is, for a given solution, independent of the volume of solution being frothed. If the initial volume, however, falls below a certain value this is no longer true

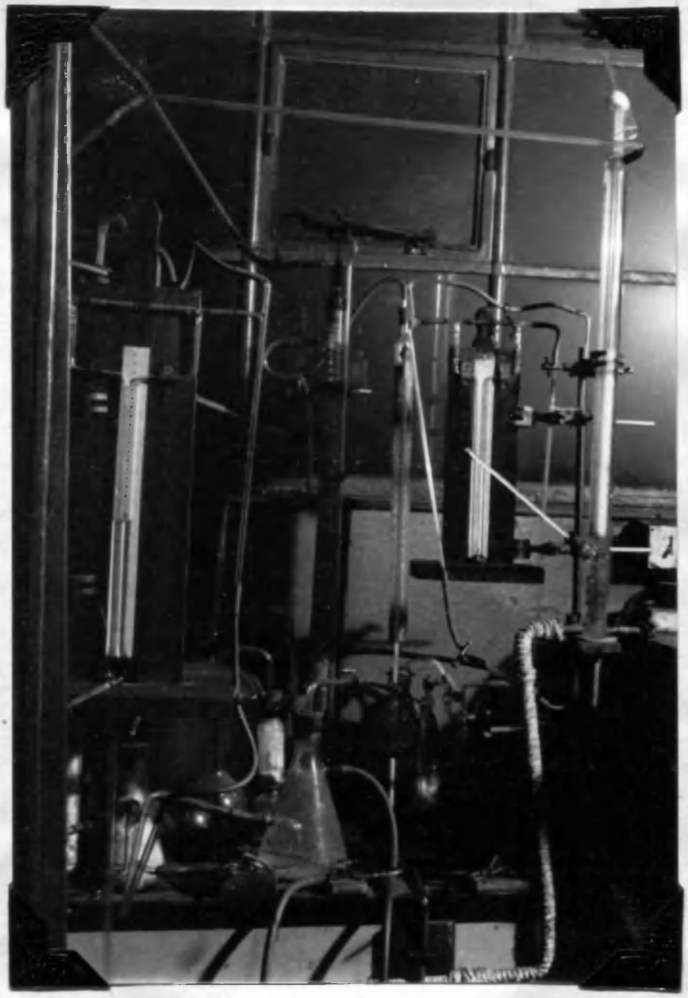


Photo. 5.

Frothing Apparatus No. 5.

The frothing tube is on the extreme right of the photograph.

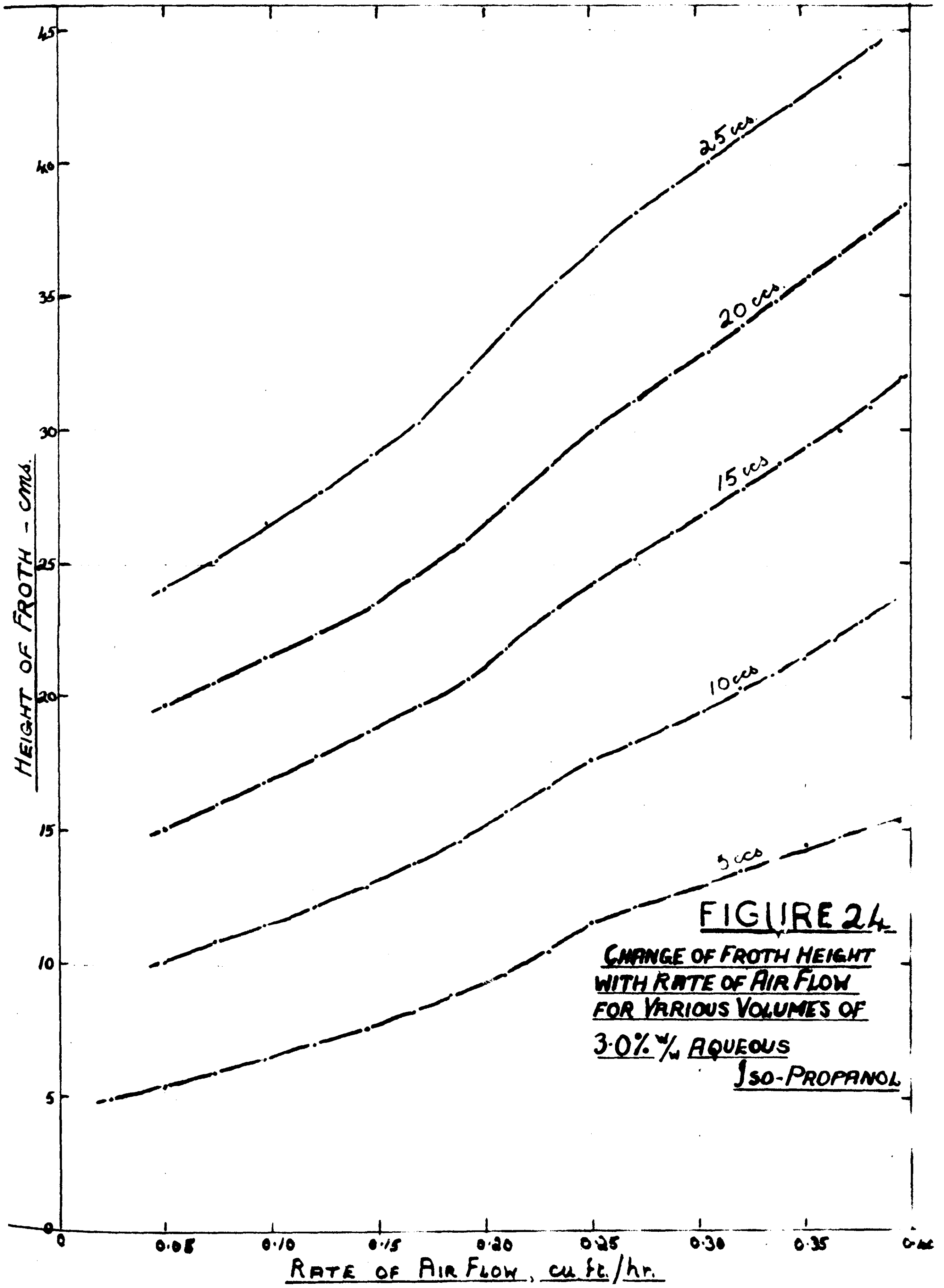


FIGURE 24

CHANGE OF FROTH HEIGHT WITH RATE OF AIR FLOW FOR VARIOUS VOLUMES OF 3·0% w/w AQUEOUS ISO-PROPANOL

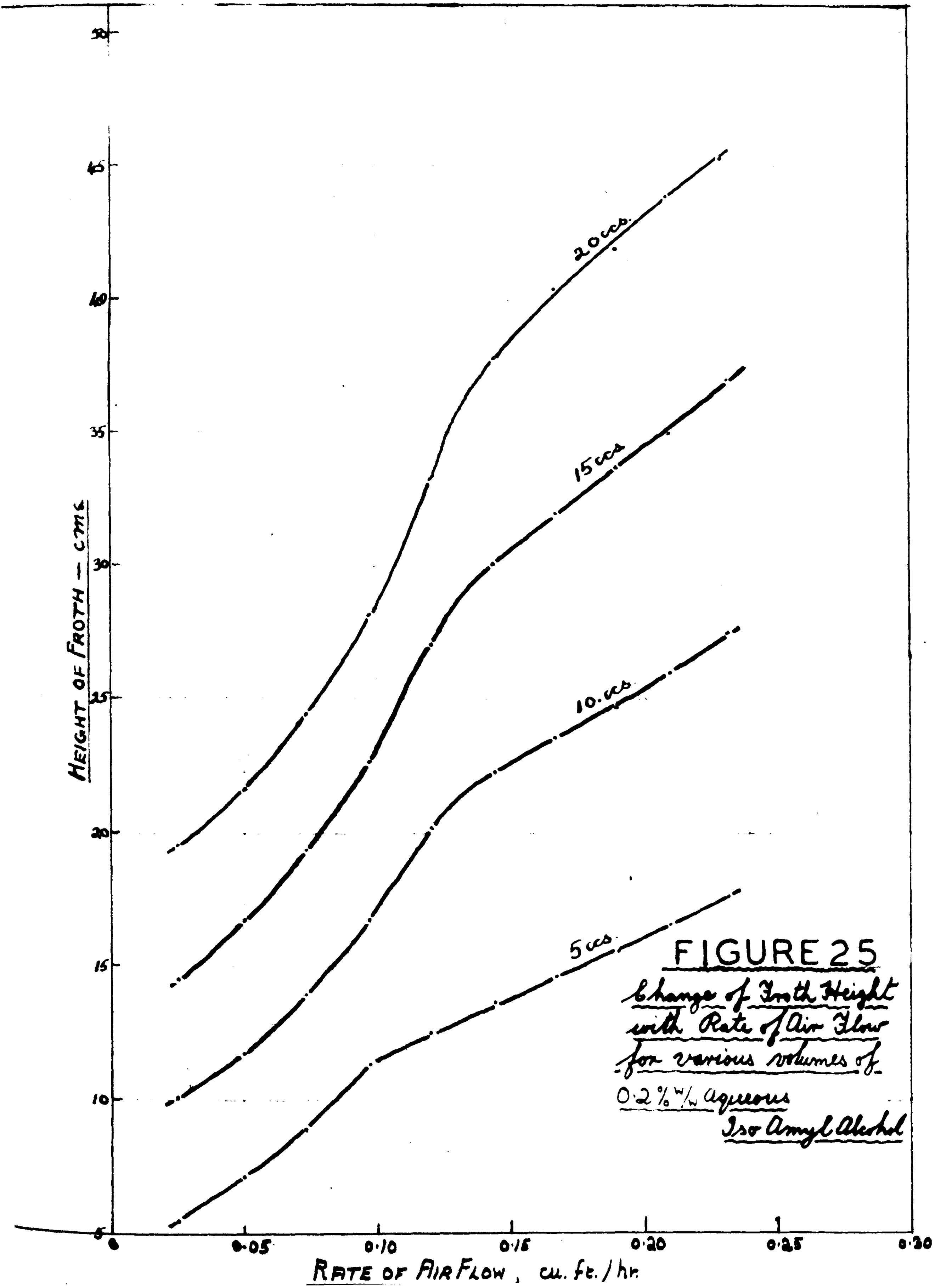


FIGURE 25

Change of Froth Height with Rate of Air Flow for various volumes of 0.2% w/w aqueous Iso Amyl Alcohol

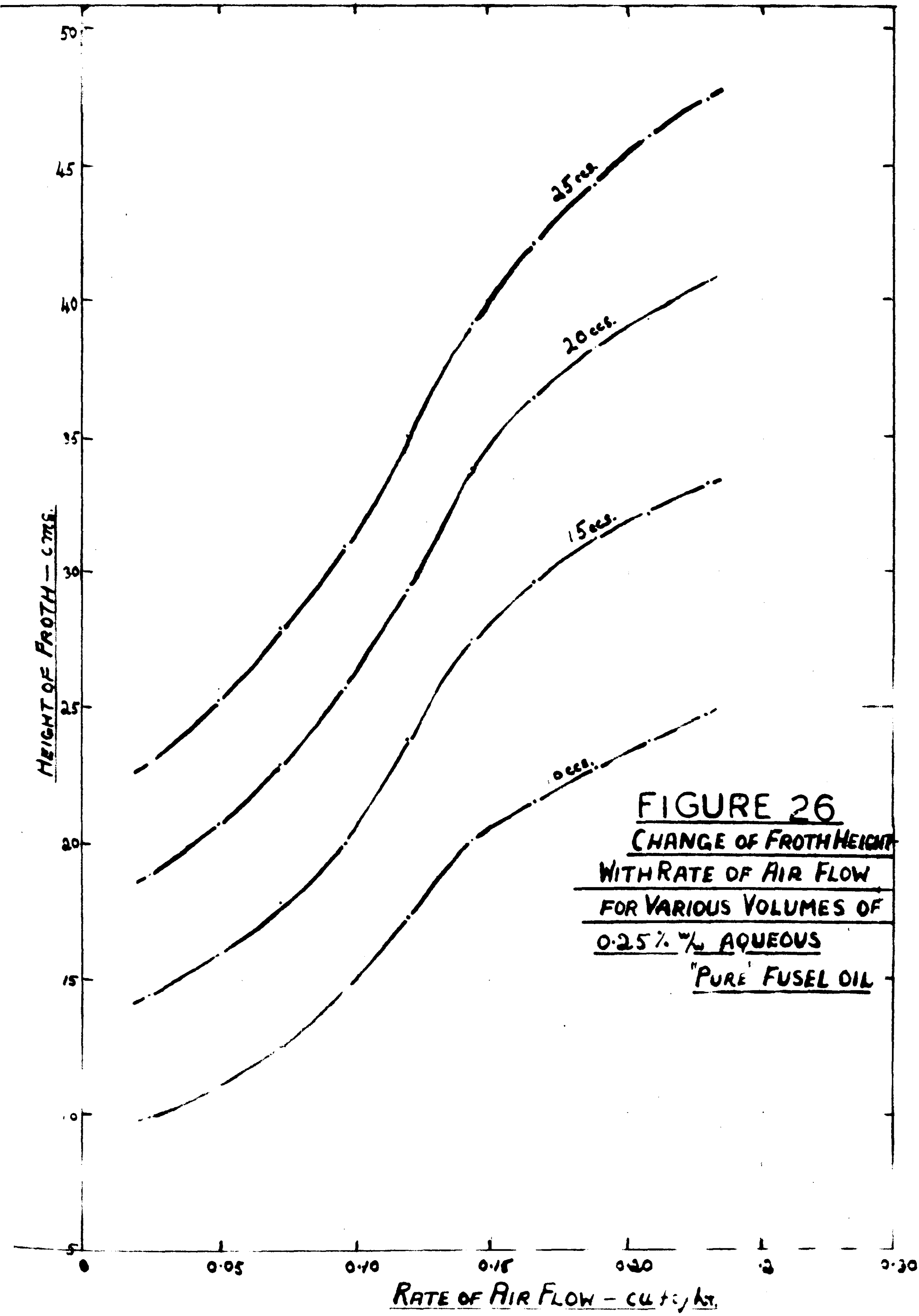


FIGURE 26
CHANGE OF FROTH HEIGHT WITH RATE OF AIR FLOW FOR VARIOUS VOLUMES OF 0·25% w/w AQUEOUS "PURE" FUSEL OIL

as can be seen from the 5 cc. curve in Figure 25. Bikerman's postulates were only fulfilled for "large" volumes of solution. It is here considered therefore that 100 ccs. solution in Frothing Apparatus No. 3 and No. 4, and 20 ccs. solution in Frothing Apparatus No. 5 were "large" volumes. It is shown later that the position of the discontinuity is dependent on the rate of formation of the froth column and is thus dependent on the dimensions of the apparatus.

(3) The curve below the discontinuity is not a straight line. This is the range covered by Bikerman. Thus his law $v = \Sigma V$ is merely an approximation to the truth.

It has been suggested above that curves below the discontinuity follow the law

$h' = k' V^2$ ----------------------------(13a)

In Figure 26A froth height (h') is plotted against (V^2) for the results of Figures 25 and 26 up to the discontinuity flow-rate. They form a series of straight lines. Equation No.13a therefore appears to be a general one for solutions frothed at low rates of flow in this type of apparatus. The values of the constant in Equation No. 13a for these solutions were calculated and are tabulated below.

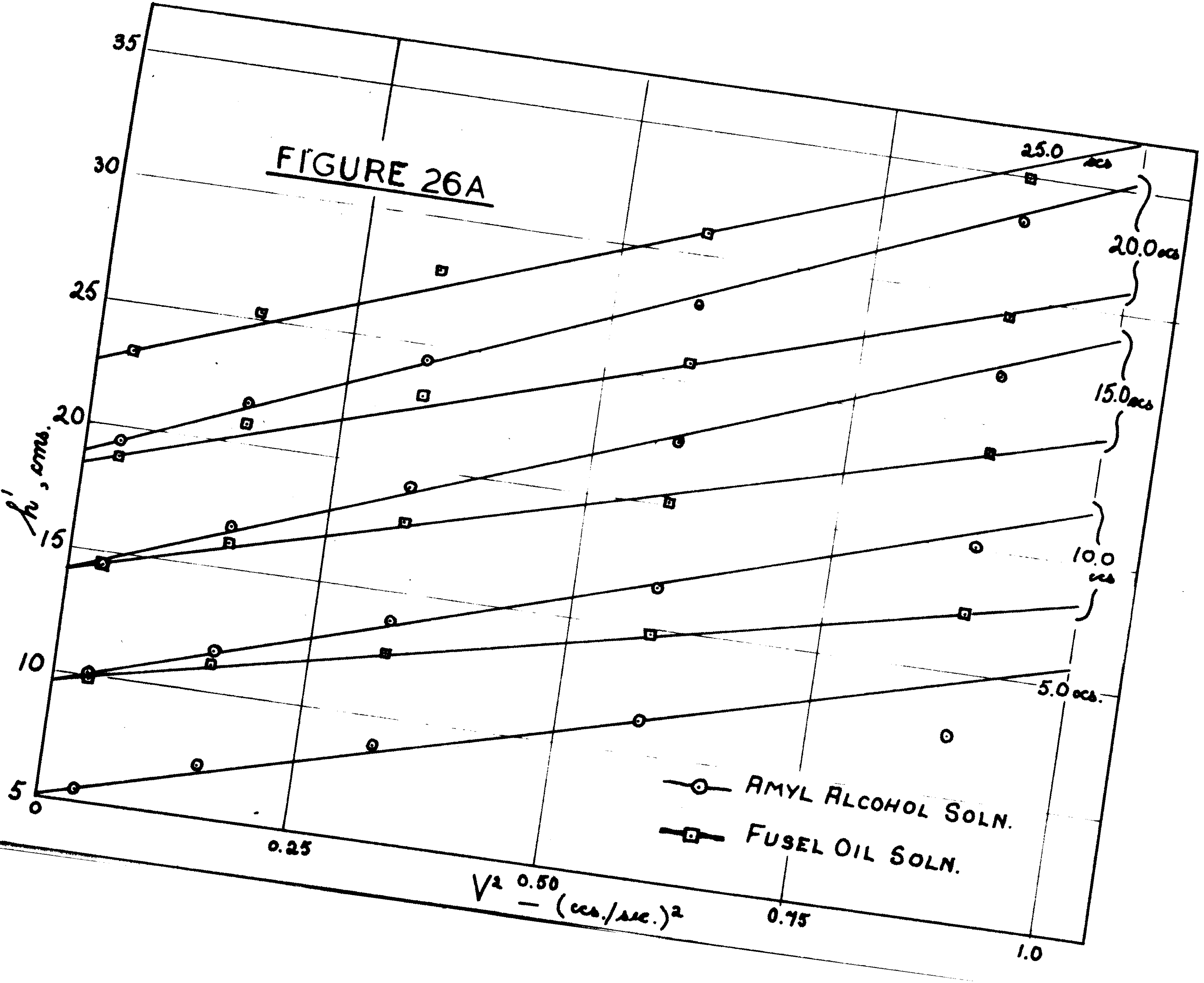


FIGURE 26A

35
30
25
20
15
10
5
h', cms.
0
0.25
0.50
0.75
1.0
V² — (ccs./sec.)²
25.0 ccs
20.0 ccs
15.0 ccs
10.0 ccs
5.0 ccs.
Amyl Alcohol Soln.
Fusel Oil Soln.

Table II.

Initial Volume (ccs.)	0.2% Isoamyl Alcohol k'	h°_{1}	h_{1}	0.25% Fusel Oil k'	h°_{1}	h_{1}
5.0	10.8	5.1	4.40	-	-	-
10.0	12.4	9.7	8.66	8.6	9.7	8.66
15.0	15.0	14.2	12.85	10.8	14.2	12.85
20.0	16.6	18.9	18.10	12.8	18.4	17.10
25.0	-	-	-	14.6	22.6	21.30

The actual height (h_{1}) of the initial volume which could be read off at the start of each test is included in the table for the sake of comparison with the virtual height (h°_{1}), the ordinate intercepts of the lines of Figure 26A. It can be seen that the gradient (k') increases regularly with initial volume, the rate of increase being 1.6 units per 5 ccs. for the isoamyl alcohol solution and about 2.0 units per 5 ccs. for the Fusel Oil solution.

(4) The curve above the discontinuity is linear. This is shown best in Figures 24 and 25. It appears therefore that Bikerman's law holds in this region, though it is doubtful if he studied froths in such an advanced state of dispersion. The gradient of this linear portion also seems to increase with initial volume of solution. It may become constant at larger initial volumes. The equation takes the form:

$$h' = k V + K \text{ ----------------------- } (14)$$

The value of the intercept (K) depends on the initial volume of solution and on the frothing power. (k) should not be confused with the earlier square law constant (k'). The values of (k) for the solutions of Figure 25 are given in Table III. The units have been rationalised.

Table III.

0.2% Iso-Amyl Alcohol.

Initial Volume:-	5 cc.	10 cc.	15 cc.	20 cc.
$k \left(\frac{cm}{ccs./sec} \right)$	5.72	7.36	9.53	10.05
$k' \left[\frac{cm}{(ccs./sec)^2} \right]$	10.8	12.4	15.0	16.6
C (ccs./sec.)	0.530	0.594	0.636	0.607

It was thought that the ratio of the constants might be independent of initial volume, i.e.

$$k/k' = C$$

This new constant has the dimensions of a rate of flow, i.e. (ccs./sec.), and from the volumes given in the above Table it seems to be less influenced by the initial volume of solution.

(5) The greater the frothing power of the solution, the smaller the rate of flow at which the discontinuity occurs. Cf. Figs. 24 and 25. This might be a convenient method of characterising frothing solutions.

(6) While Figs. 22 and 24 are of results from comparatively poor frothing solutions, Figs. 25 and 26 are results for solutions of the froth stability value necessary in flotation

practice. These latter curves are limited at the upper end, by the rate of flow value corresponding to the limiting froth height. For poor frothers this occurs at high rates of flow, for good frothers at low rates of flow. Thus for the solutions in which we are most interested (Fig. 25 and 26) the length of curve available is the shortest. This is unfortunate and is most evident in Fig. 26 giving results for a solution of pure Fusel Oil. With increase in initial volume it can be seen that the transition constituting the discontinuity takes place over a wider range of air flow rate. With the 20 cc. and 25 cc. curves for this solution the straightness of the line above the discontinuity has barely time to develop before the curve is stopped by the disintegration of the column above the limiting froth height.

Variation in the Position of the Discontinuity with Froth Stability.

It was suggested above that the position of the discontinuity with reference to the rate of air flow axis might be used as a means of characterising the frothing properties of a solution.

A test with distilled water was carried out in No. 5 Frothing Apparatus. The air bubbles which would have formed a froth in the case of a frothing solution merely increased the volume of the water. The new water height was measured for different rates of air-flow. The results are plotted for various initial volumes of water in Fig. 27. The curves

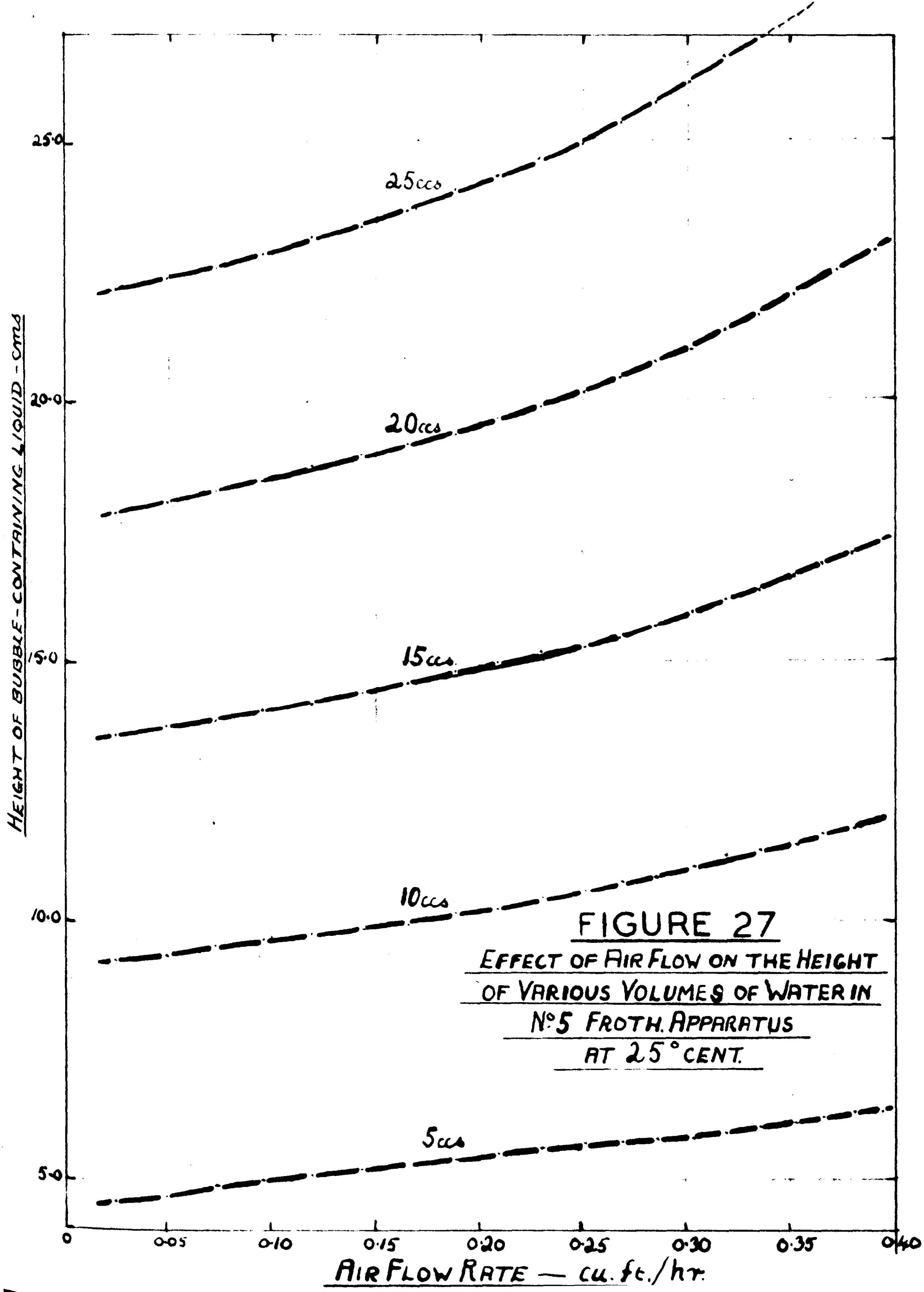


FIGURE 27

EFFECT OF AIR FLOW ON THE HEIGHT OF VARIOUS VOLUMES OF WATER IN Nº5 FROTH. APPARATUS AT 25° CENT.

show no discontinuity. The discontinuity previously obtained is thus a property of the frothing solution and not of the apparatus. It is not shown by non-frothing solutions.

A sample of pure iso-amyl alcohol was obtained (distilling between 130.5° and 131.5°C) and solutions of various concentration were prepared in double distilled water. 20 ccs. of each concentration value were frothed at various rates of flow of air in No. 5 Frothing Apparatus. The temperature of the solutions was in all cases 25 ± 0.2°C. The height of froth obtained at each rate of flow value was measured and the results plotted as in Fig. 28.

Similar solutions of Tert. Butanol (sample distilled between 82.0° and 82.5°C) were prepared and frothing tests carried out in the same way. The results for this alcohol are in Figure 28A.

A study of the curves in Figs. 28 and 28A shows that for solutions of high froth stability, i.e. iso-amyl alcohol solutions, the exact position of the discontinuity is difficult to determine. There seems in most cases just to be a gradual transition from the curve below the discontinuity to that above it (e.g. 2.5% iso-amyl alcohol). In the case of solutions of moderate froth stability, i.e. Tert-Butanol solutions the exact position of the discontinuity can be determined by producing the two portions of each curve to a sharp intersection. (See dotted intersections on the curves of Figure 28A). Although this is not a very exact process the lower curve of Figure 28B was obtained by plotting the air flow values of the discontinuities against frothing agent concentration. The upper curve in the same diagram is a reproduction of one of the Froth Stability/Concentration curves for solutions of similar strength obtained as described in a later section of this work. The two curves show an inverse similarity to each other and indicate that the discontinuity air flow rate of a solution is inversely proportional to its froth stability. As a method, however, of determining froth stability it would be difficult to apply owing to the inexact method of determining the position of the discontinuity.

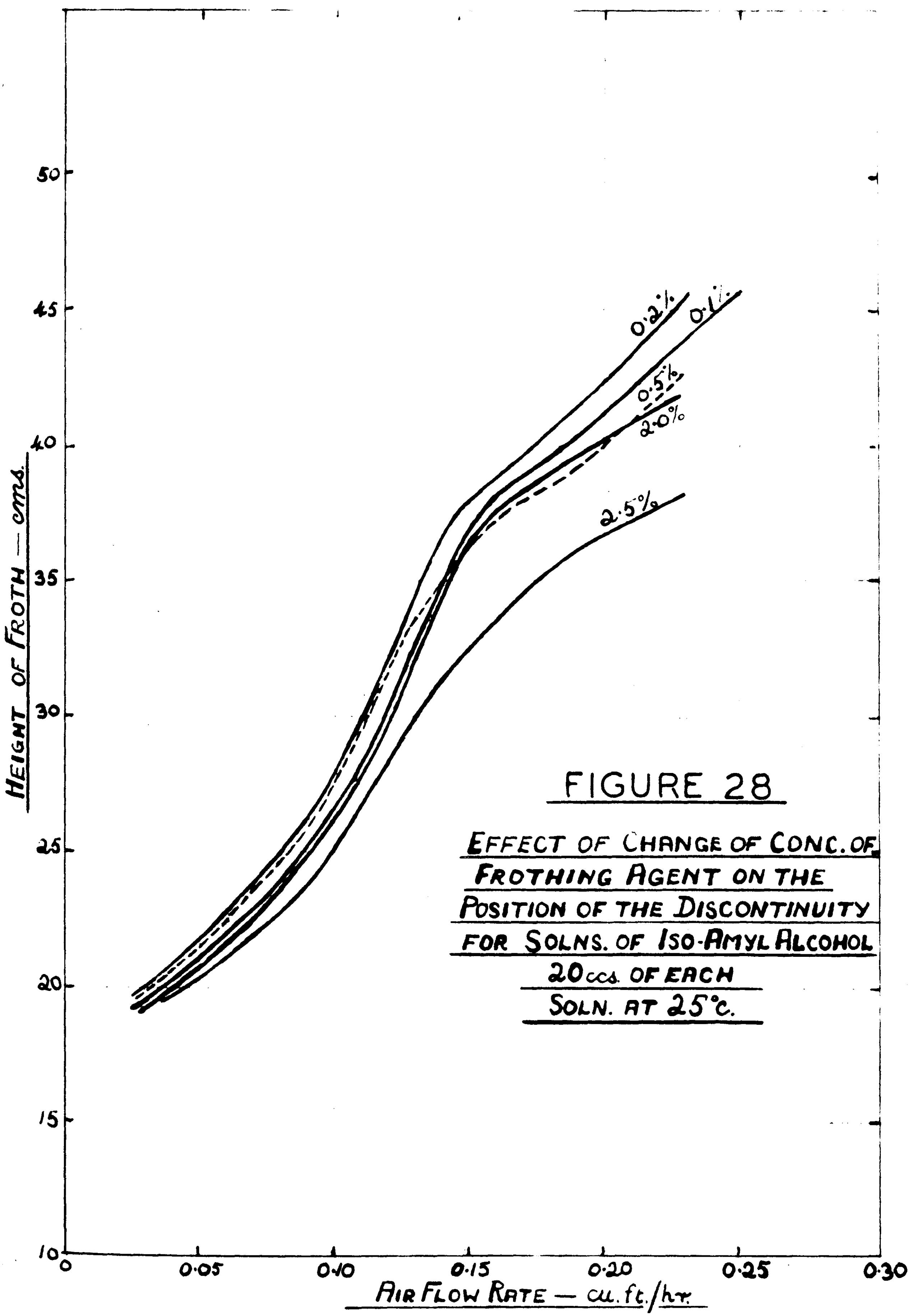


FIGURE 28

EFFECT OF CHANGE OF CONC. OF FROTHING AGENT ON THE POSITION OF THE DISCONTINUITY FOR SOLNS. OF ISO-AMYL ALCOHOL 20 ccs. OF EACH SOLN. AT 25°C.

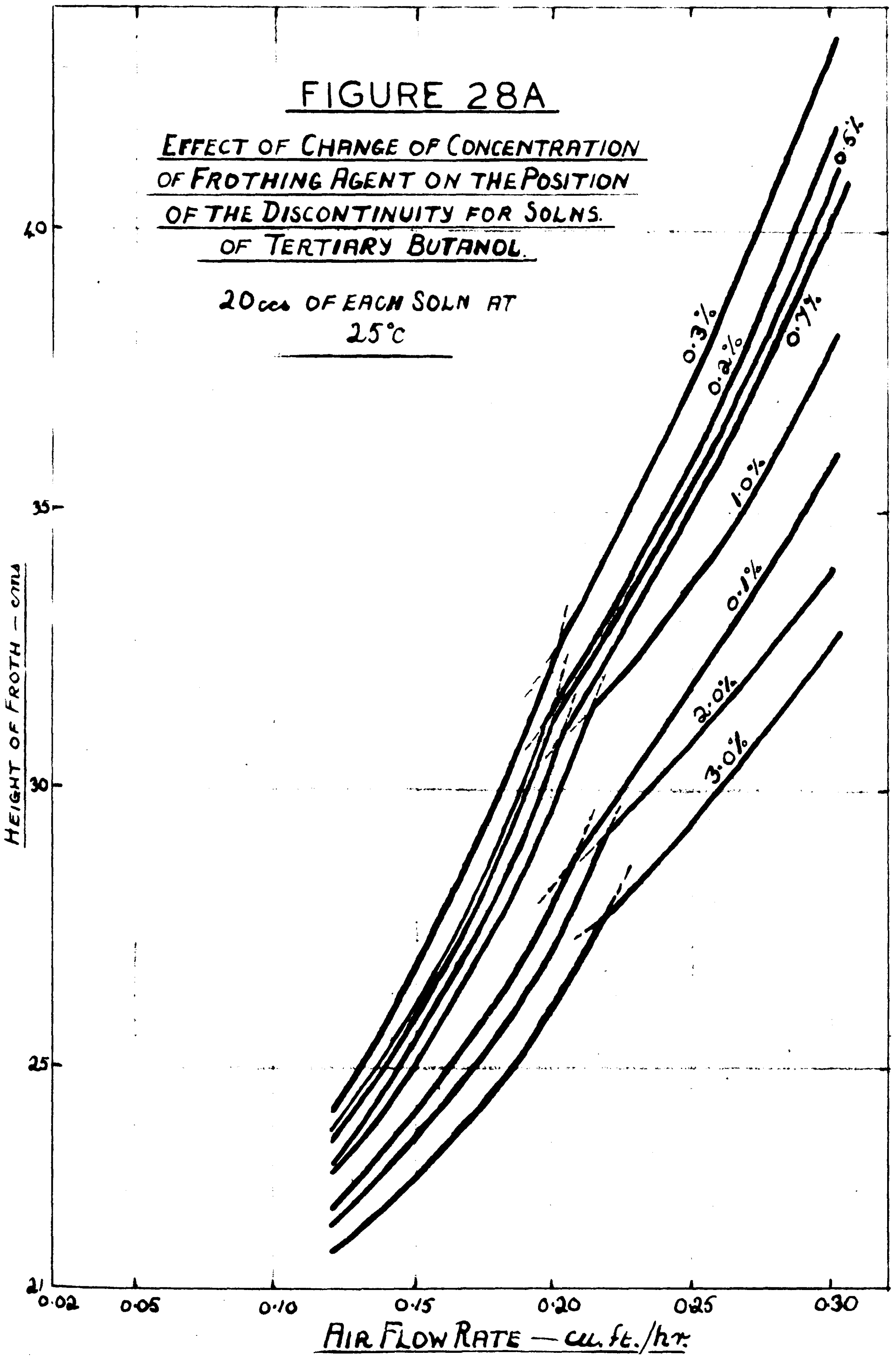


FIGURE 28A

EFFECT OF CHANGE OF CONCENTRATION OF FROTHING AGENT ON THE POSITION OF THE DISCONTINUITY FOR SOLNS. OF TERTIARY BUTANOL.

20 ccs OF EACH SOLN AT 25°C

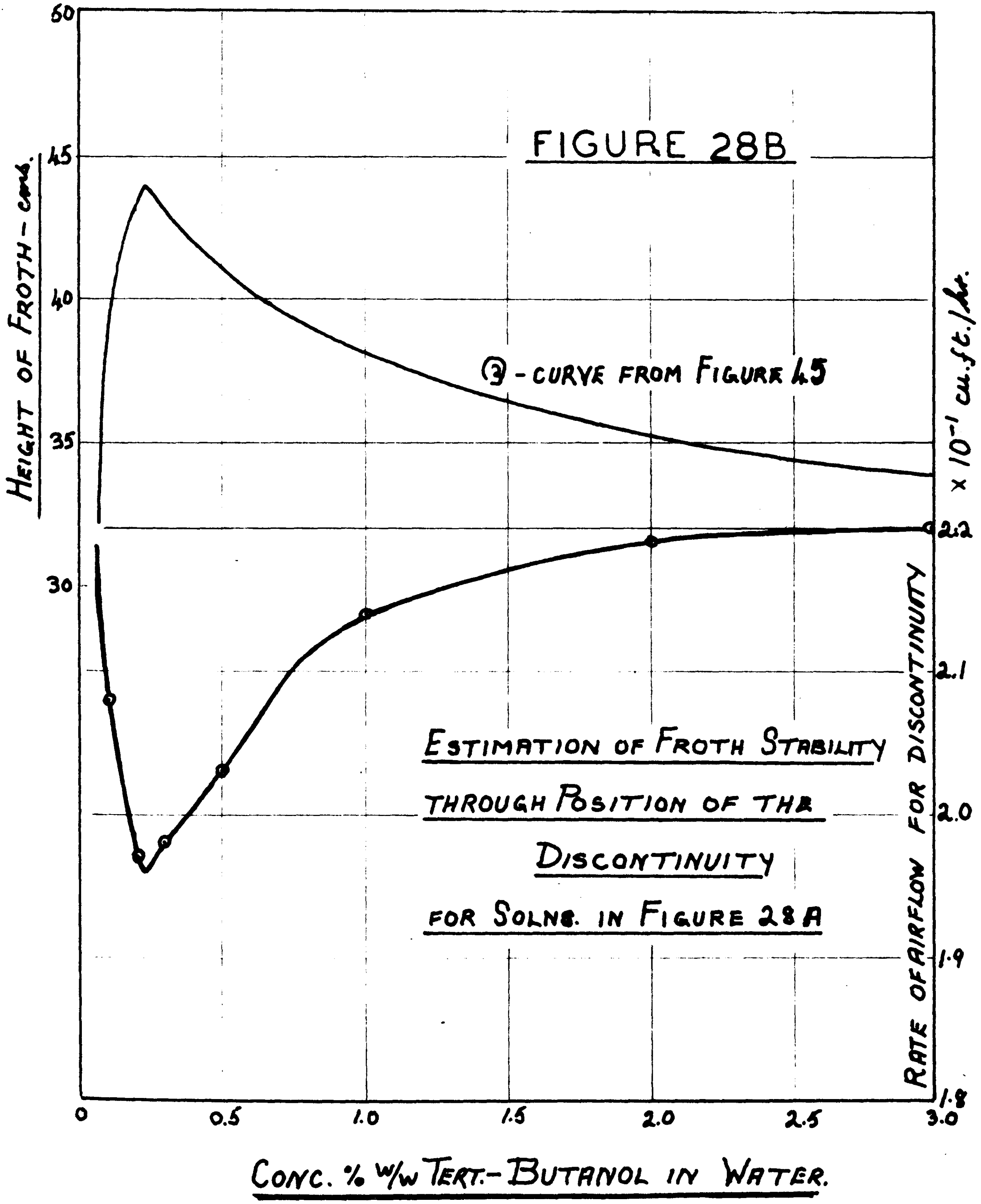


FIGURE 28B

ESTIMATION OF FROTH STABILITY THROUGH POSITION OF THE DISCONTINUITY FOR SOLNS. IN FIGURE 28A

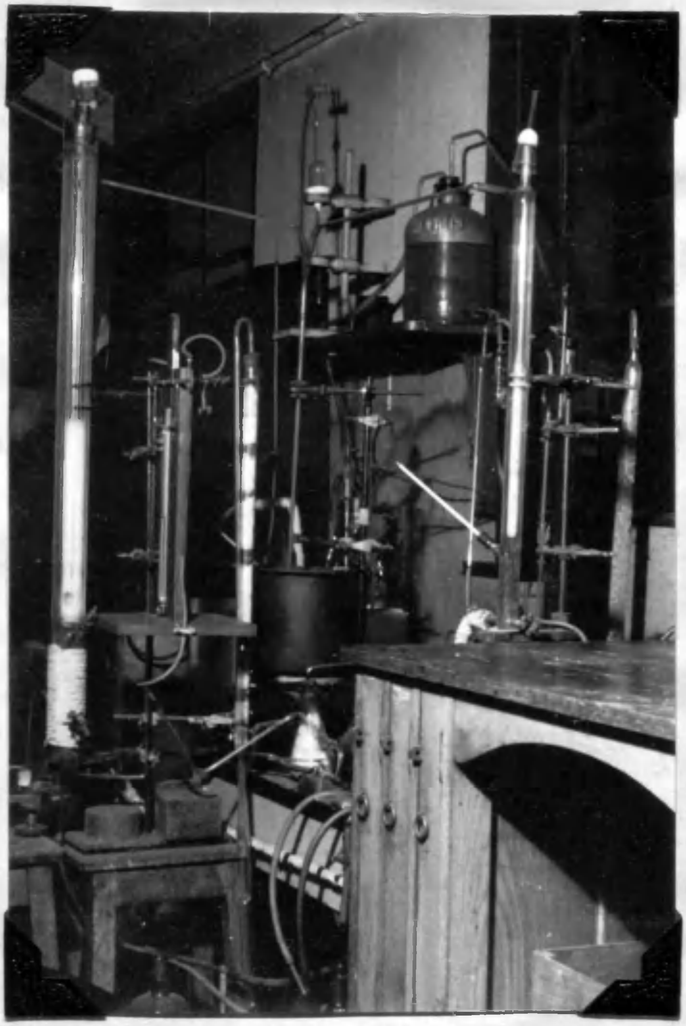


Photo. 6.

Frothing Apparatus Nos. 4 and 5.

In this case the apparatus is viewed from the reverse direction to that of Photo. 4.

Variation of length of actual foam column with rate of flow of air.

Up till now "height of froth" was taken as the total height reached by froth and bubble-containing liquid for any given rate of flow. As explained previously at low rates of flow of air the demarcation line between froth and liquid is quite visible but disappears at high rates of flow. With the No. 5 apparatus by viewing the column from the side it was quite possible to measure the position of this line with reference to the height scale. A powerful light placed behind the froth column helped to show it up in cases where its position was difficult to estimate.

This measurement was therefore made for a number of solutions of the various alcohols simultaneously with the height of froth measurements, and the results plotted. A typical result is shown in Fig. 29, for 25 ccs. of 0.4% tertiary butanol solution. The upper curve is the usual height of froth curve, showing the change in position of the top of the froth column; the lower curve is that for the change in position of the demarcation line between froth and liquid. Thus the vertical distance between the lines at any point is the length of the actual froth column.

It can be seen from Fig. 29 that the lower curve rises to a maximum value then falls away rapidly and disappears as all the liquid is virtually turned into froth. The shape of the lower curve may be explained as follows:-

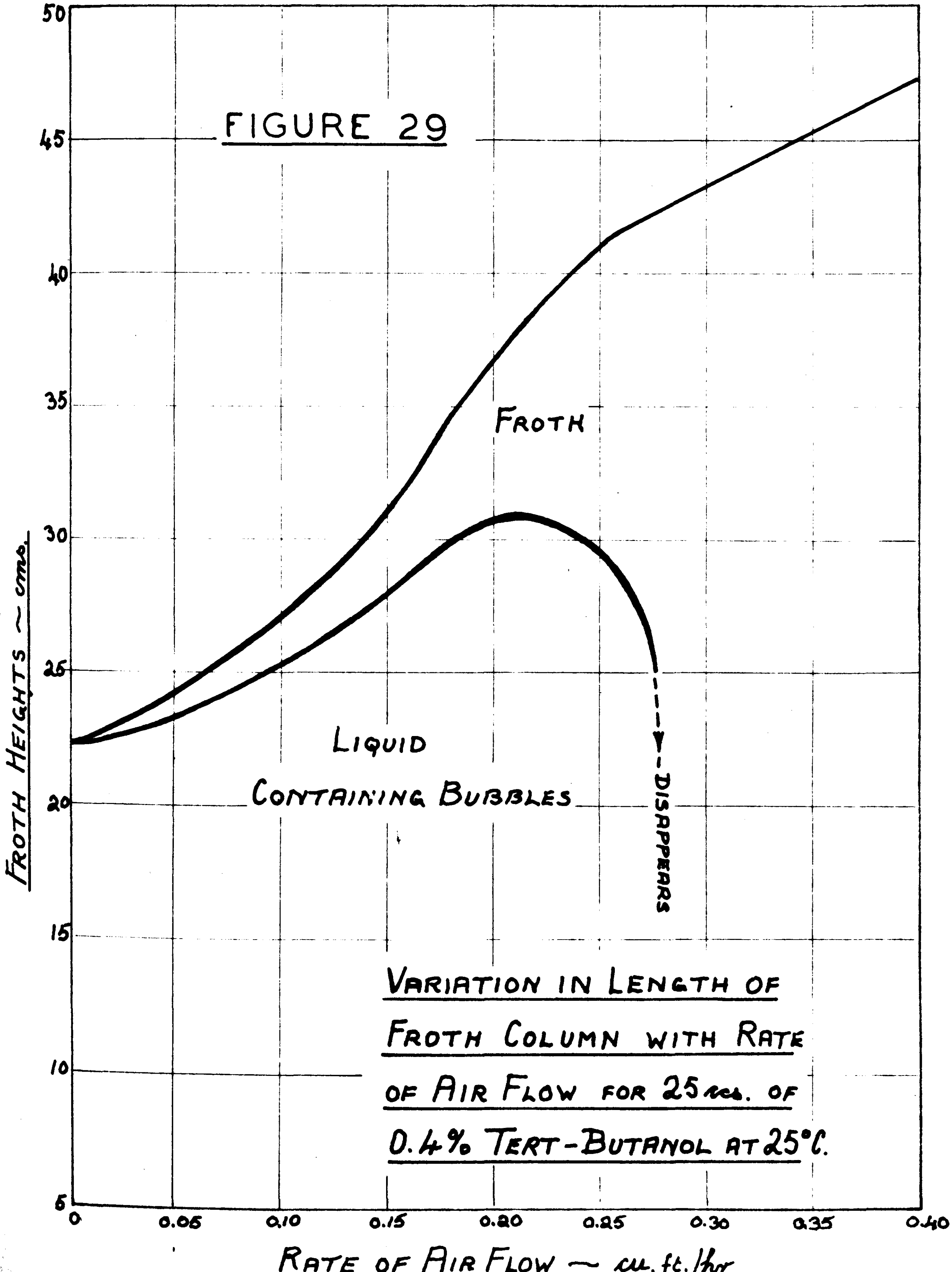


FIGURE 29

VARIATION IN LENGTH OF FROTH COLUMN WITH RATE OF AIR FLOW FOR 25 ccs. OF 0.4% TERT-BUTANOL AT 25°C.

The volume of the liquid is at first increased by the bubbles passing through it and therefore its height increases with the rate of air-flow. Were it a non-frothing liquid, it would continue to do so, but at the same time the volume is being decreased by the amount being taken up to form the bubble films of the froth. This secondary effect increases rapidly, becomes equal to the first effect at the maximum, and then becomes greater than it, causing the curve to descend again. As the rate of flow further increases, the difference between the number of bubbles per unit volume of froth and of liquid becomes so small that the line finally disappears.

It can be seen at once from the Figure that the discontinuity occurs at the point where the liquid column becomes completely dispersed as froth. Thus the portion of the curve below the discontinuity refers to a column of liquid containing bubbles and having a head of froth in dynamic equilibrium, while the portion above the discontinuity refers to a more or less homogeneous froth column also in dynamic equilibrium.

The variation in the length of the froth column for various initial volumes of solution is an interesting point. The table below shows the value of this length at various rates of flow for various initial volumes of 0.4% Tert. Butanol solution in No. 5 Frothing Apparatus.

Table IV.

Rate of Air Flow cu.ft./hr.	Length of Froth Column (cms.) for an Initial Volume of:-				
	5ccs.	10ccs.	15ccs.	20ccs.	25ccs.
0.025	0.7	0.7	0.7	0.6	0.6
0.050	1.3	1.0	1.2	0.9	1.2
0.073	1.8	2.0	2.1	1.8	1.9
0.097	2.3	2.0	2.1	1.8	1.9
0.120	3.1	2.7	2.5	2.2	2.3
0.143	-	3.5	3.5	2.9	3.1
0.167	-	4.6	4.5	3.7	5.0
0.189	-	6.2	5.1	4.9	5.4
0.210	-	7.7	7.1	6.9	7.1
0.232	-	8.9	8.4	9.6	9.3
0.252	-	-	10.9	-	11.6
0.270	-	-	16.8	-	15.9

The blanks in the table are due to the disappearance of the demarcation line. Considering the experimental difficulties involved it can be stated as shown by the table that the length of froth column produced at any rate of flow is independent of the initial volume of liquid in the apparatus, i.e. as long as there are two distinct phases in the system, liquid and froth. This may be extended by stating that the volume of actual foam produced in a froth flotation bubble column machine, under any fixed conditions of air flow and concentration of frothing reagents, is independent of the initial volume of liquid in the apparatus.

This is only true so long as the liquid has not been completely converted into froth.

On theoretical grounds too it is evident that the volume of froth is dependent only on the number and volume of bubbles constituting it and their stability, i.e. the rate of air flow and the chemical nature of the froth solution - and not on the volume of liquid.

By plotting length of actual froth column against air-flow rate, curves are obtained of the type shown for three solutions in Figure 30. It can be seen that these are regular curves and are independent of the volume of solution undergoing frothing. The constant from the equation of such a curve could be used to characterise the froth stability of solutions.

An Equation for the Determination of Froth Stability.

Ross and his co-workers (24) obtained an empirical equation for the collapse of high stability static froths produced by mechanical means from such diverse substances as beer, wine, saponin, aerosol OT, and lauryl sulphonic acid. This is:-

$$V = V_0 e^{-kt} \text{ ----------------------- } (15)$$

where V_0 is the initial volume of foam and V is the volume remaining after time t secs. K is a constant for the given foam.

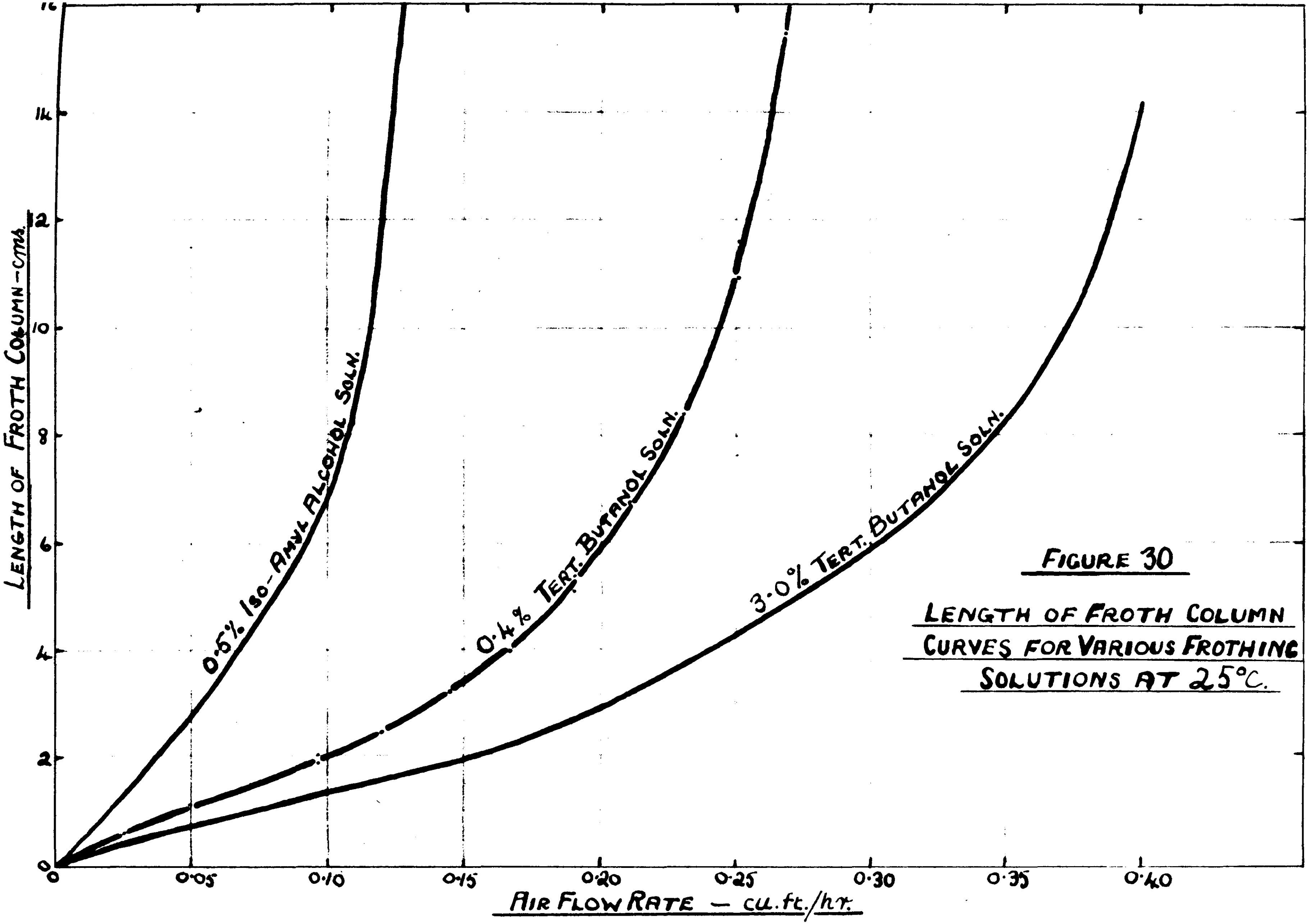


FIGURE 30

LENGTH OF FROTH COLUMN CURVES FOR VARIOUS FROTHING SOLUTIONS AT 25°C.

This formula implies that the rate of collapse of a static froth $(\frac{-dv}{dt})$ is proportional to the amount of froth present at that instant, or

$$\frac{-dv}{dt} = k.V \text{-----------------------------} (16)$$

Now in the dynamic froth system of the bubble column the volume of froth produced by a steady air flow rate increases until its rate of collapse of bubbles equals the rate of production of bubbles, i.e. rate of air flow. Thus a dynamic equilibrium is set up with a steady volume of froth when,

$$\text{Rate of air flow} = \frac{-dv}{dt}$$

Thus if equation No. 16 is true for dynamic froths we would expect that

$$\text{Rate of air flow} = k.V$$

i.e. rate of air flow is directly proportional to the volume of froth formed at that rate of flow.

This is similar to the law suggested by Bikerman, although in no case did he measure the <u>true</u> froth volume. It has, however, been shown above that as soon as the rate of air flow is increased until dispersion is complete, i.e. there is no longer bubble-containing liquid topped by a head of froth in dynamic equilibrium but a homogeneous column of froth, Bikerman's law holds. Accordingly, the law of Ross must hold. (equation No. 16). It seems therefore that the law of collapse of a froth is universal whether the collapse be in the static state or the collapsing froth be held in dynamic equilibrium by an air flow. The preliminary results of Figure 30 indicate that a froth held in dynamic equilibrium on top of the liquid from which it is formed does not follow this law. This can be due to the fact that in this condition the froth column can grow or decrease at both ends, while when the liquid is completely dispersed the froth can only grow or decrease at the upper surface.

Experimental.

An extensive series of tests was now carried out to discover a new equation connecting rate of collapse of froth with froth volume. The results given below were chosen at random from a wide range of concentrations and alcohols. The aqueous solutions were prepared as described in the later section on the variation of froth stability with concentration of reagent (see page 108). Samples of each solution (100 c.cs.) were frothed in apparatus No. 4 and (20 c.cs.) in apparatus No. 5.

An extra mm./cm. paper scale was fixed to the outside (in front and slightly to one side) of the thermostatic jacket tube of No. 4., so that, viewed horizontally, the divisions were coincident with those of the inner scale on the back of the frothing tube. A large (100 cms.) cathetometer was set vertically before No. 4 frothing tube as shown in Photograph 4. It was possible, by focusing the cross wires

Table V.

Froth Volume results for an aqueous solution containing 1.2% w/w n-Propanol at 25° ± 0.2°C.

Frothing Apparatus No. 4.

Internal cross-sectional area of tube = 7.56 ± 0.01 sq.cms.

Rate of Air Flow (litres/hr.)	Length of Froth Column (cms.)	Volume of Froth (c.cs.)	$\log_{10} V$
17.30	0.90	6.80	0.833
20.71	1.29	9.74	0.989
23.90	1.57	11.84	1.073
26.78	1.97	14.87	1.172
29.49	2.44	18.43	1.266
32.20	2.88	21.8	1.339
34.75	3.74	28.2	1.450

Frothing Apparatus No. 5.

Internal cross sectional area of tube = 1.17 ± 0.01 sq.cms.

2.12	1.8	2.11	0.324
2.80	2.4	2.81	0.449
3.46	3.2	3.75	0.574
4.14	3.9	4.57	0.660
4.80	5.1	5.97	0.776
5.47	6.6	7.73	0.882

Discussion of Results.

Since the froth column under consideration is in dynamic equilibrium, the volume rate of air flow up the column must equal the rate of destruction of froth at the top of the column, and the law of the curves in Figs. 31 and 32 may be stated generally as,

$$-\frac{dv}{dt} = f(V) \text{ ---------------------------- } (17)$$

where the R.H.S. of this equation is some function of the

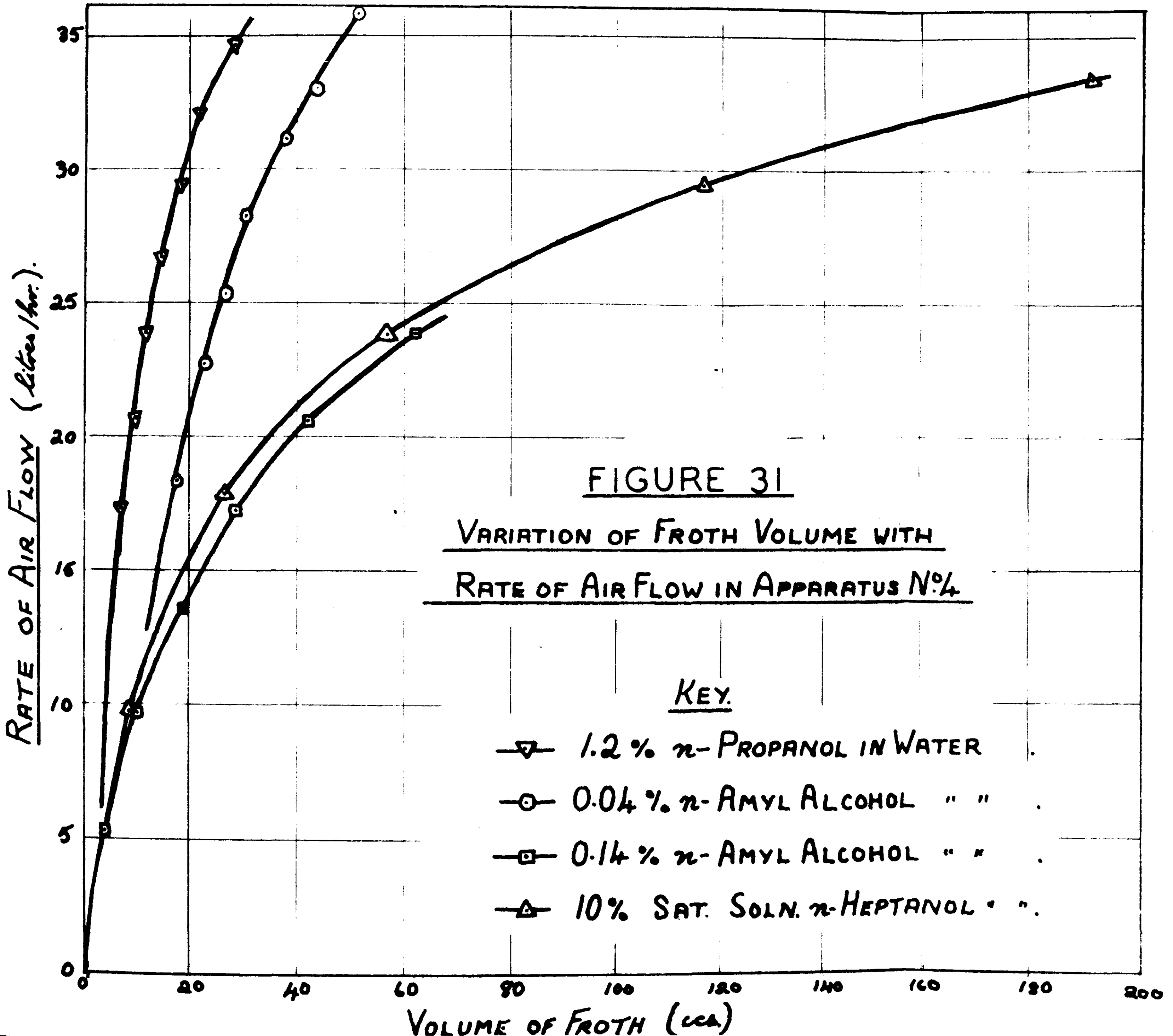


FIGURE 31

VARIATION OF FROTH VOLUME WITH RATE OF AIR FLOW IN APPARATUS Nº4

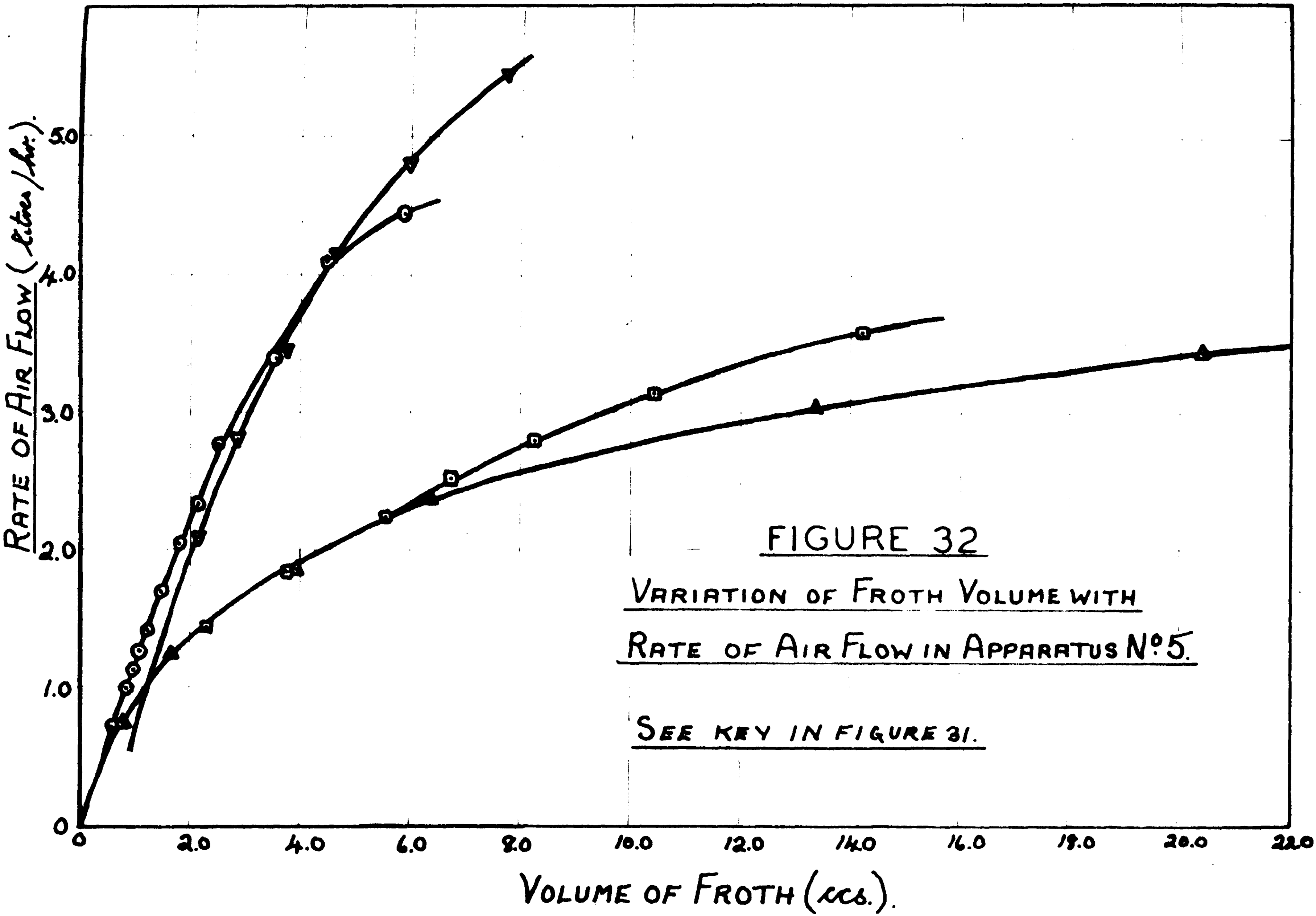


FIGURE 32

VARIATION OF FROTH VOLUME WITH RATE OF AIR FLOW IN APPARATUS Nº 5.

SEE KEY IN FIGURE 31.

volume of froth. The shape of the experimental curves suggests a logarithmic function, so the $\log_{10}$ of each value of froth volume was evaluated as shown in Table V, and the rate of air flow plotted against $\log_{10} V$ as shown in Figures 33 and 34. It can be seen that a linear plot is obtained for nearly the whole of the range chosen. The only divergencies occur at very low rates of air flow (See dotted portion of curve for 0.04% n-amyl alcohol solution in Figure 34), i.e. at rates less than about twelve litres per hour for No. 4 and less than about two litres per hour for No. 5. This is due to the fact that zero rate of air flow demands zero froth, whereas the law followed by the straight lines,

$$-\frac{dv}{dt} = b \log V + a \text{ ---------------------- } (18)$$

where *a* and *b* are constants, cuts zero rate of flow at a definite volume *not* equal to zero but given by

$$b \lg V = -a$$

$$\therefore \quad \log V = -\frac{a}{b} = \log (1 - c), \quad \underline{c} \text{ being a constant.}$$

$$\therefore \quad V = (1 - c) \text{ c.cs,}$$

i.e. around seven c.cs. for the tests carried out in No. 4. and around one cc. for No. 5.

The initial non-linear portion would seem therefore to indicate the transition to dynamic equilibrium reached at about 12 litres/hr. for Frothing Apparatus No. 4 and 2 litres/hr. for No. 5. Since the constants *a* and *b* are independent of initial volume of solution they would seem to be suitable for characterising frothing solutions.

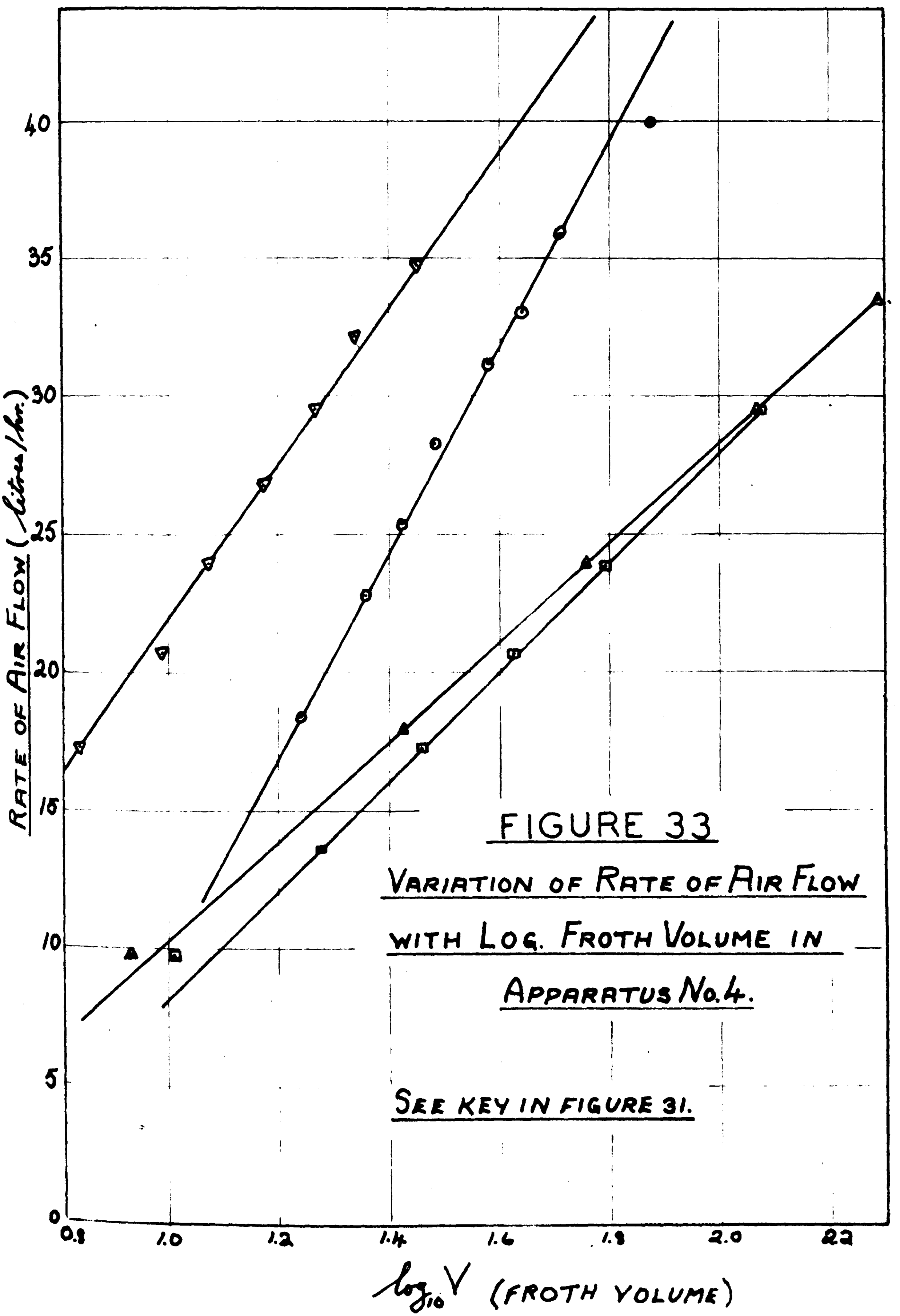


FIGURE 33

VARIATION OF RATE OF AIR FLOW WITH LOG. FROTH VOLUME IN APPARATUS No. 4.

SEE KEY IN FIGURE 31.

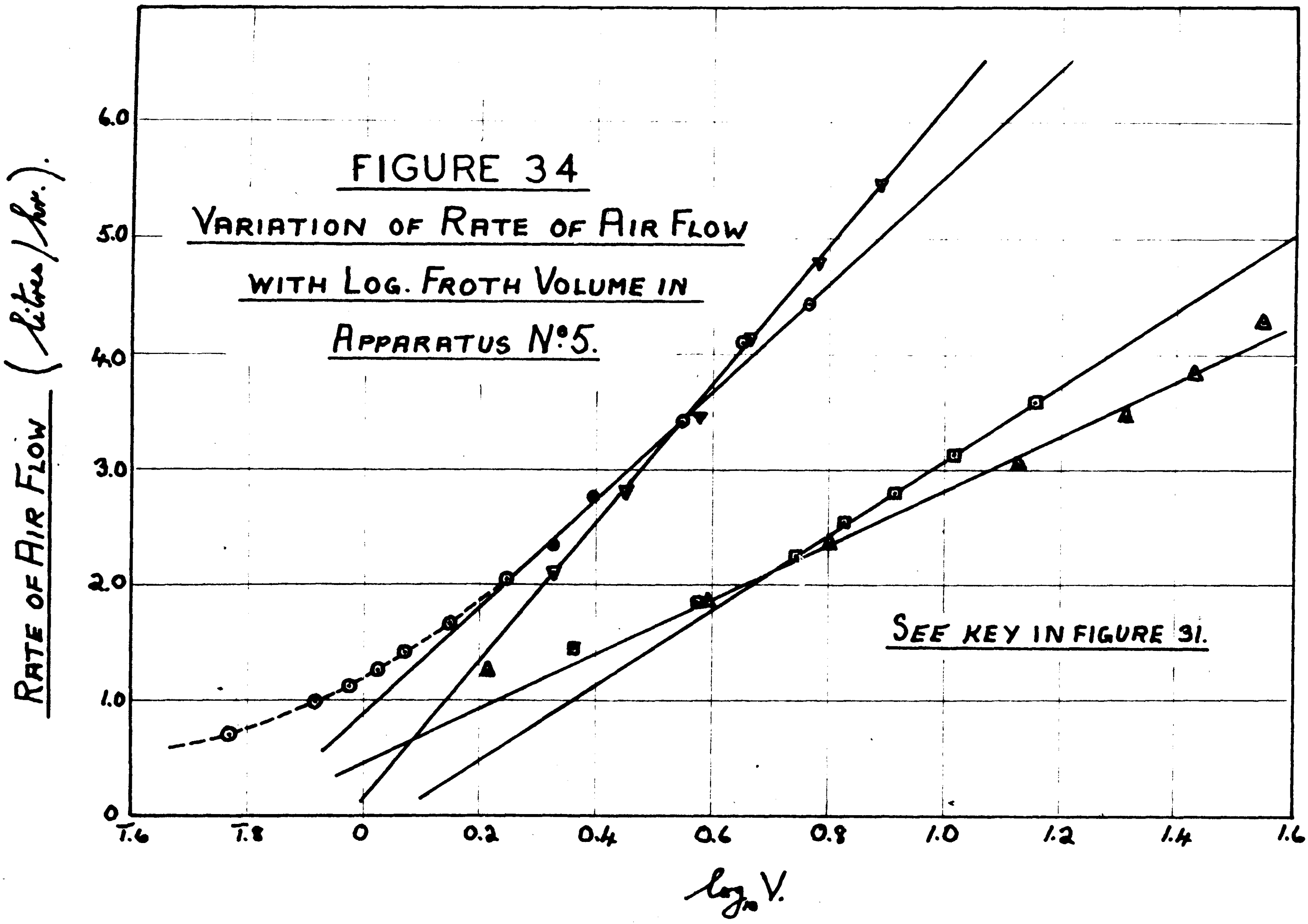


FIGURE 34

VARIATION OF RATE OF AIR FLOW WITH LOG. FROTH VOLUME IN APPARATUS N°5.

The values of a and b taken from Figs. 33 and 34 are given below in Table VI. In calculating the constants the unit of rate of air flow has been changed from (litres/hr.) to the more rational (c.cs./second).

Table VI

Froth Volume Constants.

Alcohol	Conc. in Aqueous Soln. (% w/w)	Constants For No. 4,		Constants For No. 5.		Ratio of Gradi (b/b)
		a	b	a	b	
n-Propyl	1.2	-1.79	7.88	4.12×10^{-2}	1.67	4.72
n Amyl	0.04	-7.71	10.32	24.4×10^{-2}	1.29	8.00
	0.14	-3.25	5.51	-4.73×10^{-2}	0.903	6.10
n-Heptyl	0.018	-2.16	5.02	12.4×10^{-2}	0.659	7.61

The units of constant a are c.cs. per second, and of b are c.cs. per second per log. cc. The above table shows that they are not independent of the dimensions of the apparatus. Although no obvious connection can be seen between the values of the intercept A for a given solution in No. 4 and No. 5, the ratio pf the gradient of the linear plot for the solution in No. 4 to that in No. 5 (i.e. b for No. 4/b for No. 5) is approximately constant, and is given as the last column of Table VI. The mean value of this ratio above (6.61) is very near the ratio of the cross-sectional areas of the frothing tubes, i.e. cross-sect. area No. 4/cross-sect. area No. 5

7.56/1.17 = 6.46

If it is postulated that under ideal conditions of measurement these ratios are equal, the gradient (b) of Equation No. 18 must contain a factor equal to the cross-sectional area of the frothing tube, i.e. if $b = mA$ where A is the cross-sectional area of tube and m is a new constant, equation No. 18 becomes

$$-\frac{dv}{dt} = mA \log V + a$$

If we let the volume rate of air flow up the tube be R,

then $R = -\frac{dv}{dt}$ and

$$\frac{R}{A} = m \log V + n \text{ ---------------------------(19)}$$

where $n = a/A$

If we let (-F) be the linear falling velocity of the top of the froth column, since there is a state of dynamic equilibrium, the equation becomes,

$$-F = m \log V + n \text{ ---------------------------(20)}$$

This final equation should be a universal one for a head of froth in dynamic equilibrium on top of the liquid from which it is formed, since the constants should be independent of the initial volume of solution and dimensions of the frothing tube. They would therefore warrant the term froth stability constants since they depend only on the nature of the solution being tested.

Confirmation of Hypothesis.

In order to test the above hypothesis one alcohol was chosen whose aqueous solutions cover a wide range of froth

Table VII

Variation of Froth Volume with **Rate of Air Flow** for **solutions of Sec.-Heptanol at 25°C.** in Frothing Apparatus No. 4.

Rate of Air Flow (litres/hr.)	Percentage Saturation of Solution in Water.							
	5.0%		10.0%		20.0%		30.0%	
	Vol.(c.cs.)	$\log_{10} V$	Vol.(c.cs.)	$\log_{10} V$	Vol.(c.cs.)	$\log_{10} V$	Vol.(c.cs.)	$\log_{10} V$
5.36	4.53	0.656	3.10	0.491	3.62	0.559	3.78	0.578
9.77	9.74	0.989	10.42	1.018	9.74	0.989	10.95	1.040
13.62	17.97	1.255	22.95	1.361	20.85	1.319	19.79	1.297
17.30	30.1	1.479	39.2	1.593	36.3	1.560	35.8	1.554
20.71	47.6	1.678	65.5	1.816	72.6	1.861	64.6	1.810
23.90	71.4	1.854	105.4	2.023	133.4	2.125	106.9	2.029
26.78	109.0	2.037	-	-	-	-	-	-
Gradient (b)	16.88		15.50		12.50		14.21	
	40.0%		50.0%		60.0%		80.0%	
5.36	4.38	0.642	3.32	0.521	3.78	0.578	1.74	0.241
9.77	10.88	1.037	11.92	1.076	9.51	0.978	2.57	0.410
13.62	20.40	1.310	20.75	1.317	18.20	1.260	8.84	0.947
17.30	38.2	1.582	34.5	1.538	30.2	1.480	23.40	1.369
20.71	67.0	1.826	55.2	1.742	50.7	1.705	58.8	1.769
23.90	114.8	2.060	87.1	1.940	85.3	1.931	150.2	2.177
Gradient (b)	13.90		16.42		14.95		8.72	

Table VIII.

Variation of Froth Volume with Rate of Air Flow for solutions of Sec.-Heptanol at 25°C. in Frothing Apparatus No. 5.

Rate of Air Flow (litres/hr.)	Percentage Saturation of Solution in Water.							
	5.0%		10.0%		20.0%		30.0%	
	Vol.(ccs.)	$\log_{10} V$	Vol.(ccs.)	$\log_{10} V$	Vol.(ccs.)	$\log_{10} V$	Vol.(ccs.)	$\log_{10} V$
0.71	0.527	$\bar{1}.722$	0.586	$\bar{1}.768$	0.527	$\bar{1}.722$	0.527	$\bar{1}.722$
1.45	1.807	0.257	1.990	0.299	1.522	0.182	1.990	0.299
2.12	3.53	0.548	4.33	0.637	4.09	0.612	3.98	0.600
2.80	6.53	0.815	7.84	0.894	7.49	0.875	7.49	0.875
3.48	11.35	1.055	15.49	1.190	17.22	1.236	14.59	1.164
Gradient (b)	2.50		2.29		1.93		2.34	
	40.0%		50.0%		60.0%		80.0%	
0.71	0.458	$\bar{1}.661$	0.351	$\bar{1}.545$	0.410	$\bar{1}.613$	0.176	$\bar{1}.246$
0.99	0.761	$\bar{1}.881$	0.761	$\bar{1}.881$	0.527	$\bar{1}.722$	0.293	$\bar{1}.467$
1.45	1.990	0.299	2.106	0.323	1.990	0.299	0.586	$\bar{1}.768$
1.70	2.635	0.421	2.810	0.449	2.635	0.421	1.288	0.110
2.12	3.98	0.600	4.22	0.625	3.98	0.600	1.930	0.286
2.80	8.67	0.938	8.20	0.914	7.49	0.875	5.74	0.759
Gradient (b)	2.12		2.37		2.32		1.41	

Table IX.

Froth Volume Constants for Solutions of Tables VII and VIII.

Soln. strength:-		5% Sat.	10%	20%	30%	40%	50%	60%	80%
Apparatus No. 4	(b)	4.69	4.31	3.48	3.95	3.86	4.57	4.16	2.42
	(a)	-2.10	-2.07	- 0.714	-1.35	-1.28	-2.19	-1.35	+1.49
Apparatus No. 5	(b)	0.695	0.637	0.537	0.651	0.589	0.659	0.645	0.392
	(a)	22.2×10^{-2}	21.2×10^{-2}	30.4×10^{-2}	21.1×10^{-2}	22.8×10^{-2}	18.0×10^{-2}	21.2×10^{-2}	48.1×10^{-2}
Gradient Ratio (b/b)		6.76	6.78	6.48	6.08	6.57	6.94	6.45	6.19
Intercept Ratio(a/a)		-9.47	-9.77	-2.35	-6.41	-5.63	-12.21	-6.38	+3.09

Mean value of gradient ratio = 6.53

Ratio of apparatus cross-sectional areas = 6.46 sq.cms.

Units of b on above table = ccs./second/log cc.

Units of a in above table = ccs./second.

that the ratio of the gradients is constant and equal to the ratio of the cross-sectional areas of the frothing tubes within the limits of experimental error. On the other hand the ratio of the intercepts is subject to wide variation. It is evident that the actual value of the intercept will depend on the rate of flow at which the transition to the linear law is complete. This transition period will not only be dependent on the frothing power of the solution but will also be a function of the dimensions of the frothing apparatus. Equation No. 20 therefore appears to be verified as a fundamental relationship for a frothing tube.

Although the form of the equation, in which (-F) is used to signify the downward linear velocity of the top surface of the froth, is the more fundamental one, equation No. 19 is a more convenient form for calculation. It may be put into the more general exponential form as follows:-

$$\frac{R}{A} = m \log V + n$$

$$= (m \log e) \log V + n$$

$$\therefore \frac{R}{A(m \log e)} - \frac{n}{m \log e} = \log_e V$$

$$\therefore V = Ne^{\frac{MR}{A}}$$

$$\text{where } N = e^{\frac{-n}{m \log}} = e^{-2.303 \frac{n}{m}}$$

$$\text{and } M = \frac{1}{m \log e} = \frac{2.303}{m}$$

The values of Table IX have been used to calculate (m), (n), (M), and (N) as shown in Table X. As predicted, for most of the aqueous solutions, there is good agreement between the value of (M) given by apparatus No. 4 and that given by apparatus No. 5. On the other hand, for any solution, the two apparati give widely different values of (N). This makes the latter useless for comparing froth stabilities as it must still be a function of the dimensions of the apparatus. Since, however, the constant (M) is now only dependent on the nature of the frothing solution it may be given the title, Froth Volume Stability Constant.

If we assume that high froth stability is associated with a large increase in froth volume per unit increase in rate of air flow, (M) from its mode of derivation will increase with froth stability. The change in (M) from solution to solution of Table X is not very great. This is due more to the fact that these solutions have rather similar froth stabilities than that (M) is insensitive to change in froth stability.

The Froth Volume Stability Constant (M) of any solution is therefore obtained by measuring in a frothing tube the volume of froth produced by a current of air at various rates of flow up to the disappearance of the demarcation line between the froth and bubble-containing liquid, and then determining the gradient (b) of the plot of rate of air flow

TABLE X

Further Constants for solutions of Tables VII & VIII.

Soln. strength:-		5% Sat.	10%	20%	30%	40%	50%	60%	80%
Apparatus No.4	(m)	0.621	0.571	0.461	0.523	0.511	0.604	0.550	0.320
	(n)	-0.278	-0.274	-0.0944	-0.178	-0.169	-0.290	-0.178	+0.197
	(M)	3.71	4.04	5.01	4.41	4.52	3.82	4.19	7.21
	(N)	2.81	3.02	1.60	2.19	2.14	3.03	2.11	0.242
Apparatus No.5	(m)	0.594	0.544	0.459	0.557	0.503	0.563	0.552	0.335
	(n)	0.190	0.181	0.260	0.180	0.195	0.154	0.181	0.411
	(M)	3.88	4.24	5.02	4.14	4.58	4.09	4.18	6.89
	(N)	0.479	0.468	0.271	0.474	0.409	0.532	0.470	0.0594

$m = \frac{b}{A} =$ cm./sec./log cc. $\quad n = \frac{a}{A} =$ cm./sec.

$M = \frac{2.303}{m} =$ log cc. sec. cm.^{-1}

$N = e^{-2.303\frac{n}{m}} \quad \therefore \quad \log N = \frac{-n}{m}$

against the logarithm of the froth volume. Then

$$M = \frac{2.303\ A}{b} \quad \text{--------------------------} (21)$$

where the symbols have the same significance as above.

The variation of (M) with concentration of frothing agent is discussed later.

The Rational Approach to the Bubble Column.

The complexity of the bubble column problem and the large number of variables involved make a rigorous mathematical analysis extremely difficult, if not impossible. The empirical relationships, however, of equations No. 12, 13 and 14 give some indication of how the variables are related. These have been used in conjunction with a dimensional analysis of the variables to derive the more fundamental formulae given below.

The problem is best divided into two sections, (a) that covered by equation No. 13a, where we have a head of froth on top of a column of bubble-containing liquid, what might be termed the "two-phase" system, and (b) that covered by equation No. 14, where the column of bubble-containing liquid has disappeared, what might be termed the "homogeneous" system.

(a) the "two-phase" system.

In the formation of a vertical cylindrical column of froth on top of a column of bubble-containing liquid, by blowing air into the base of a liquid column through a sintered disc, the following variables are likely to be involved.

h', the height of froth above the initial head (h_1) of liquid on sintered disc.

i.e. $h' = H - h_1$

ρ, the density of the column averaged over its total length, (i.e. from top of froth to sintered disc). Thus, if density of the liquid in the column is $\underline{x}$ gms./cc., and density of gas in the bubbles is $\underline{x}_1$ gms./cc.,

$$\rho = \frac{xh_1 + x\,(H - h_1)}{H}$$

$\frac{dP}{dH}$, the pressure gradient up the column. This variable is non-uniform since the pressure gradient up the bubble-containing liquid column must be relatively high and that up the froth relatively low, but it may be averaged as was (ρ) above,

i.e. $\frac{dP}{dH} = \frac{P}{H} = \frac{\rho g H}{H} = \rho g$

where g is the acceleration due to gravity.

V, the linear velocity of air bubbles up the column,

i.e. $V = -F$ of equation No. 20

$= \frac{R}{A}$ of equation No. 19

μ, the viscosity between bubble films and between bubbles and the tube wall.

S, the surface tension of the liquid.

It is supposed that this analysis is carried out at constant temperature. (25°C).

Then for the bubble column there is some function of these variables equal to zero.

i.e. $f(h', \rho, \frac{dP}{dH}, V, S) = 0$

According to Buckingham's Π theorem (43), if these six variables are described by three fundamental dimensional units (Length, L; Mass, M; and Time, T.), they may be grouped into three dimensionless terms, there being only four variables to each term. Only one of these need be changed from term to term.

In the following, three of the variables (h', ρ, V) have been selected to be common to all terms. These were assigned the unknown exponents a, b, c, etc., while for convenience the remaining variables were given the exponent -1.

Then if the non-dimensional groups are symbolised by Π

$$\phi(\Pi_1, \Pi_2, \Pi_3) = 0 \text{ ------------------------ } (22)$$

and $\Pi_1 = h'^{a_1} \rho^{b_1} V^{c_1} \left(\frac{dP}{dH}\right)^{-1}$

$$\Pi_2 = h'^{a_2} \rho^{b_2} V^{c_2} \mu^{-1}$$

$$\Pi_3 = h'^{a_3} \rho^{b_3} V^{c_3} S^{-1}$$

Each non-dimensional group may be assembled by replacing the variables with their dimensional equivalents, e.g. in Π_1

$$(L)^{a_1} \left(\frac{M}{L^3}\right)^{b_1} \left(\frac{L}{T}\right)^{c_1} \left(\frac{M}{L^2T^2}\right)^{-1} = L^0 M^0 T^0$$

L: $a_1 - 3b_1 + c_1 + 2 = 0$

M: $b_1 - 1 = 0 \quad \therefore b_1 = 1$

T: $-c + 2 = 0 \quad \therefore c_1 = 2$

$$\therefore a = -1$$

$$\therefore \Pi_1 = \left[\frac{\rho V^2}{h' \frac{dP}{dH}}\right]$$

The remaining non-dimensional groups are obtained in the same way. Thus equation No. 22 finally takes the form

$$\phi\left(\frac{\rho V^2}{h' \frac{dP}{dH}} , \frac{h'\rho V}{\mu} , \frac{h'\rho V^2}{S}\right) = 0$$

It has been indicated on page 67 that with the froth column in this condition the height of froth is directly proportional to the second power of the rate of air flow. Thus -

$$\frac{dP}{dH} = C' . \phi'\left(\frac{h'\rho V}{\mu} , \frac{h'\rho V^2}{S}\right) . \frac{\rho V^2}{h'}$$

If it is considered that at small heads of froth, and for one particular liquid (i.e. S constant and μ constant), ϕ' is constant, $C' . \phi' = C''$

$$\frac{dP}{dH} = C'' . \frac{\rho V^2}{h'}$$

$$\therefore g\rho = C'' . \frac{\rho V^2}{h'}$$

$$\therefore h' = C'' . \frac{V^2}{g} \text{----------------------------} (23)$$

No mention has as yet been made of the effect noticed on page 68, that the gradient of the plot of height of froth against the square of the air flow rate increased with initial head of liquid. A number of experiments were carried out with pure water in the frothing tubes and it was found that the expansion produced by the rising bubbles at an-air flow rate was directly proportional to the initial liquid head and inversely proportional to the tube diameter (D). Thus equation No. 23 becomes

$$h' = Q.\frac{h_1}{D}.\frac{V^2}{g} \text{----------------------------} (24)$$

where $C'' = Q.\frac{h_1}{D}$

or $$h' = Q.\frac{h_1}{DgA^2}.R^2 \text{----------------------------} (25)$$

where Q is a non-dimensional constant which should be independent of the apparatus dimensions, and as previously

h_1, is the initial head of liquid

R, is the volume rate of air flow.

A, is the cross-sectional area of the frothing tube.

Since this relationship will only hold for small heads of froth, $Q.\frac{h_1}{DgA^2}$ is the gradient of the plot of(h') against R^2 at zero rate of flow.

The complete equation in terms of the total "height of froth" (H) above the sintered disc is then

$$H = Q.\frac{h_1}{DgA^2}.R^2 + h_1^{\cdot} \text{------------} (26)$$

where h is the virtual height of the initial liquid volume as introduced on page 63

Experimental

Froth heights for a number of dilutions of a saturated solution of Sec-Heptanol in water at a range of air-flow rates are given in Table XI. The results obtained for 100 ccs. of solution in No. 4. apparatus are compared with

Table XI.

Froth Heights for various solutions of Sec-Heptenol in Water.

Frothing Apparatus No. 4.

Rate of air flow (R) ccs./sec.	R^2	Height of Froth (H) cms. Solution - % Saturation 40%	50%	60%	80%
1.73	2.99	13.31	13.38	13.18	13.07
2.72	7.40	14.62	14.80	14.31	13.74
3.79	14.36	16.09	16.28	15.71	14.94
4.81	23.13	17.91	18.18	17.49	16.89
5.76	33.17	20.70	20.94	20.66	19.89
6.64	44.10	24.93	25.38	24.68	23.70
7.44	55.37	29.90	30.67	28.80	27.66
8.20	67.23	32.9	33.3	32.3	30.3
9.66	-	37.3	37.8	36.8	34.7
11.34	-	42.7	43.2	41.8	38.4
12.17	-	45.5	46.0	44.4	41.5
13.30	-	48.1	48.6	47.6	44.0
14.41	-	49.8	50.0	49.5	46.0
16.22	-	51.5	51.7	51.5	48.7

Frothing Apparatus No. 5.

Rate of air flow (R) ccs./sec.	R^2	40%	50%	60%	80%
0.197	0.0388	19.0	19.0	19.0	18.75
0.275	0.0756	19.65	19.7	19.6	19.3
0.403	0.162	21.3	21.4	21.2	20.6
0.473	0.224	22.2	22.3	22.2	21.7
0.589	0.347	24.2	24.3	24.1	23.3
0.665	0.442	25.8	25.9	25.4	24.5
0.778	0.605	28.1	28.4	27.9	26.6
0.839	-	30.3	31.1	29.6	27.7
0.961	-	32.9	33.9	32.3	29.0
1.150	-	35.1	36.7	34.3	30.1
1.332	-	36.6	37.3	35.8	31.3
1.519	-	37.6	38.4	36.7	32.2

those for 20 ccs. in No. 5 apparatus. All frothing tests were carried out at 25°C. The results are plotted in Figures 35 and 36. The curves take the usual shape. The plot of height of froth (H) against (R^2) for these solutions at low air-flow rates is shown in the composite figure 37A and B. As expected, the curves are only truly linear at the lowest flow rates. The values of (Q) in equation No. 26 for these solutions have been calculated from these gradients at zero flow-rate, and are shown below in Table XII.

Table XII

$$[illegible] = \frac{[illegible]}{R_2^2 - R_1^2} \quad \frac{[illegible]}{h_1}$$

Apparatus No. 4, 100 ccs. solution.

$A^2 = 57.15$ sq. cms.^{2} $D = 3.10$ cms.

$h_1 = 12.40$ cms. $g = 981$ cms/sec.^{2}

Solution Strength:	40%	50%	60%	80%
Q	2932	3012	2834	2417
h_1° cms.	13.13	13.27	12.89	12.57

Apparatus No. 5, 20 ccs. solution

$A^2 = 1.37$ sq. cms.^{2} $D = 1.22$ cms.

$h_1 = 17.4$ cms. $g = 981$ cms./sec.^{2}

Solution Strength:	40%	50%	60%	80%
Q	1760	1836	1683	1524
h_1° cms.	18.22	18.22	18.22	18.13

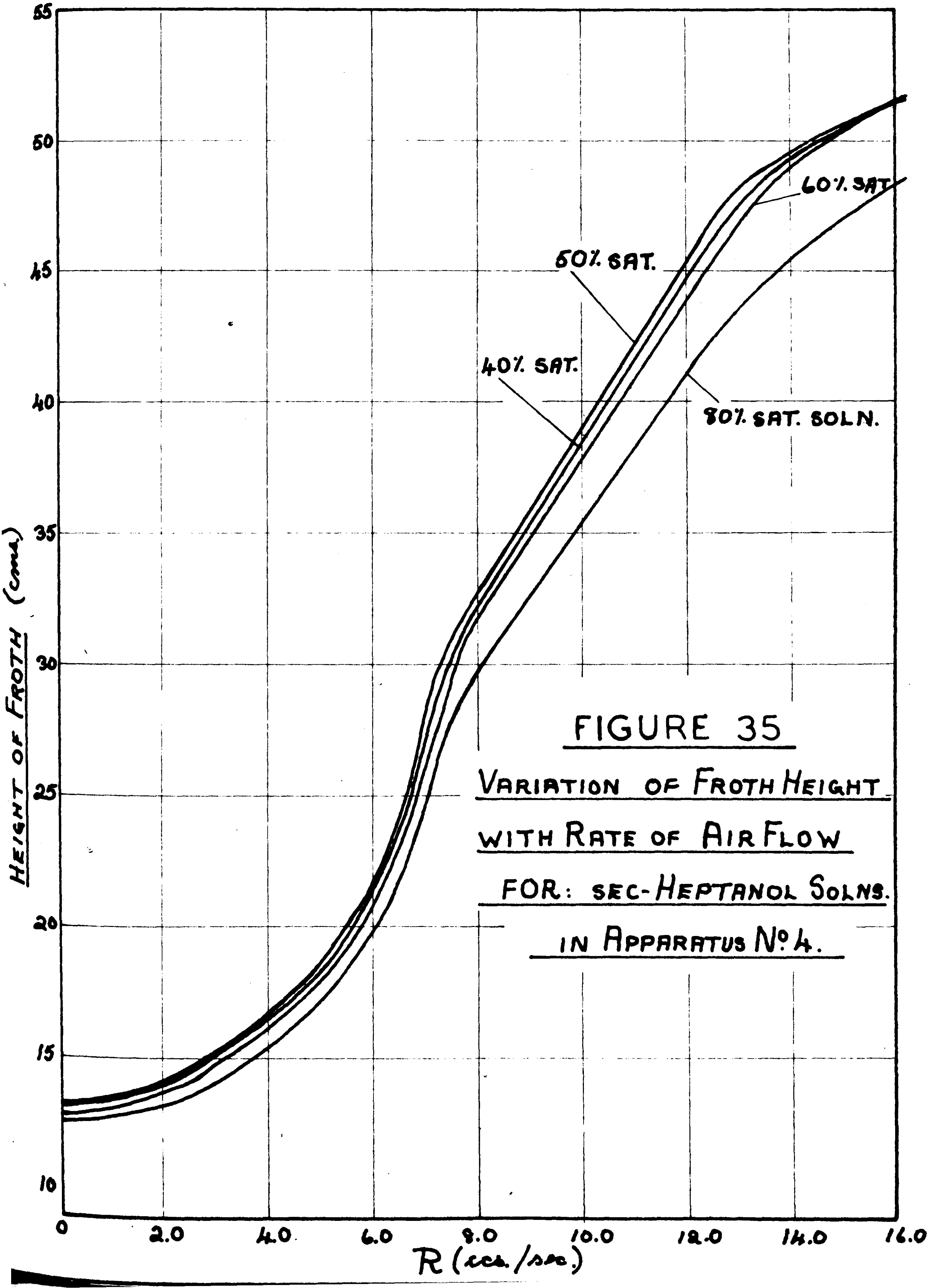


FIGURE 35

VARIATION OF FROTH HEIGHT WITH RATE OF AIR FLOW FOR: sec-HEPTANOL SOLNS. IN APPARATUS No. 4.

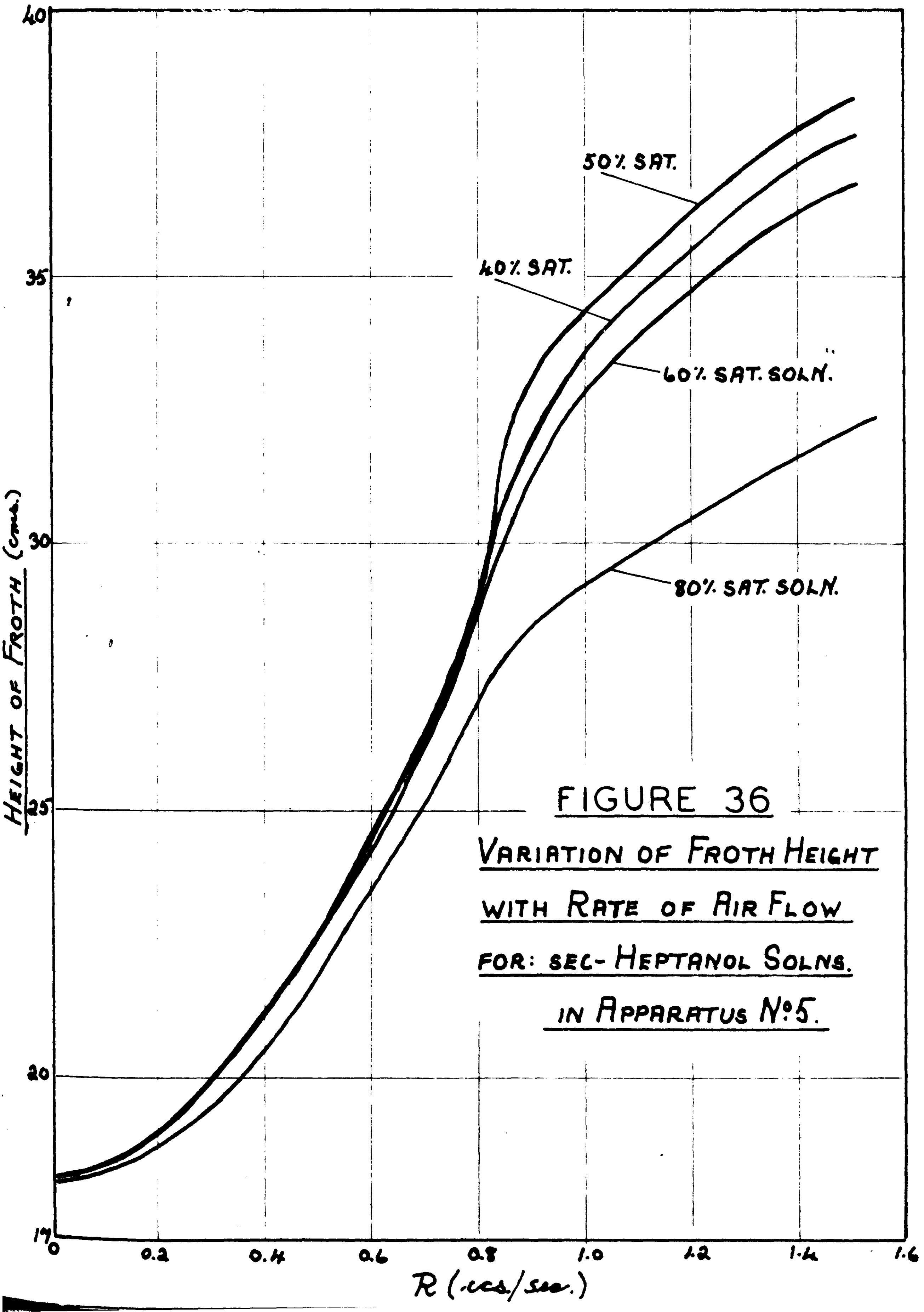


FIGURE 36

VARIATION OF FROTH HEIGHT WITH RATE OF AIR FLOW FOR: sec-HEPTANOL SOLNS. IN APPARATUS No. 5.

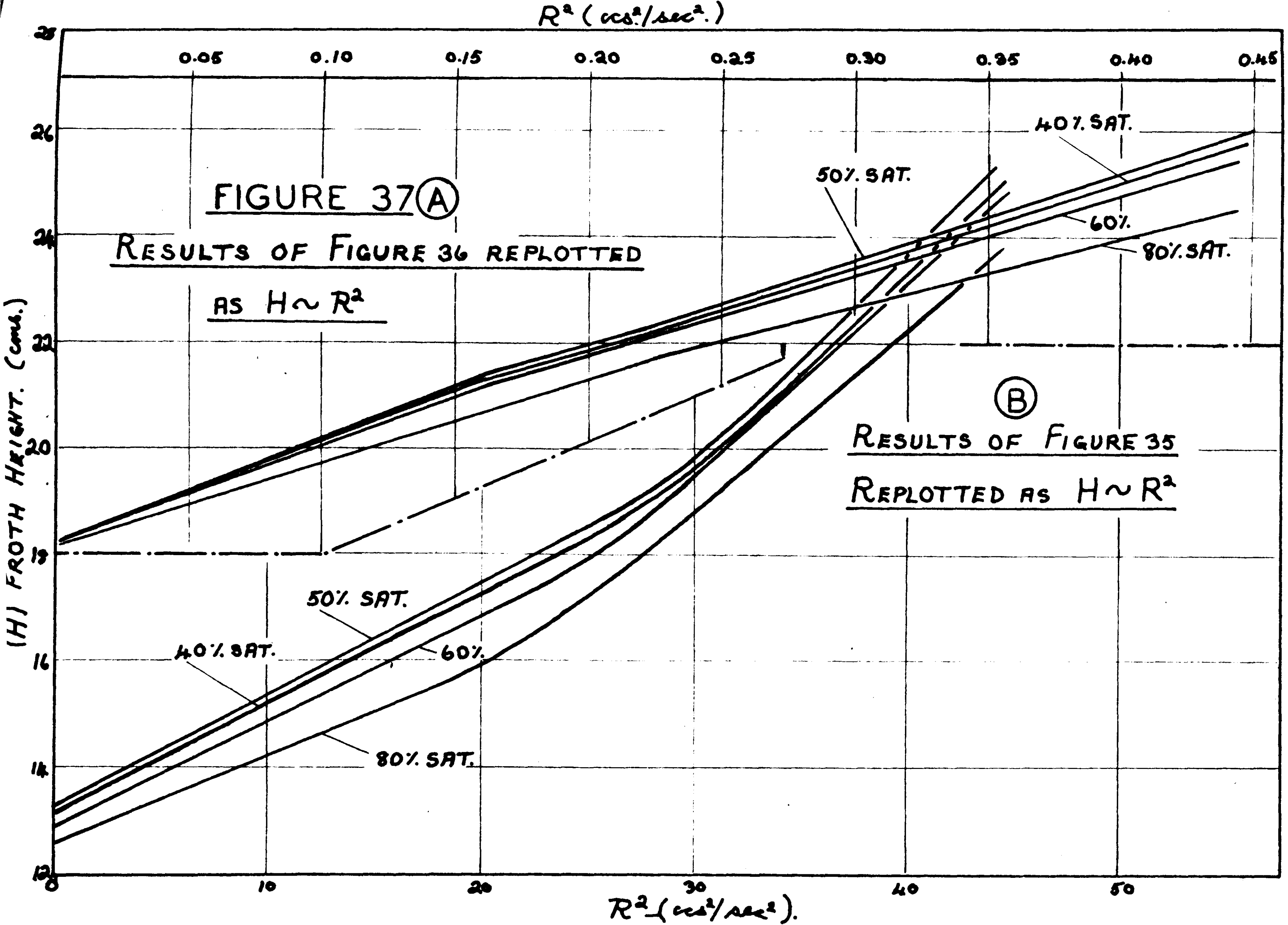


FIGURE 37 Ⓐ

Results of Figure 36 replotted as $H \sim R^2$

Ⓑ Results of Figure 35 replotted as $H \sim R^2$

Although the values of Q should theoretically be independent of apparatus dimensions the two frothing tubes do not give exactly the same value for any solution. The results, however, are of the same order and change in the same sense with concentration of frothing agent. It is thought that the porosity of the sintered disc with its effect on bubble size may be causing the discrepancy. If the porosity and average bubble size could be determined accurately, it should be possible to get values of Q giving an absolute measure of froth stability.

(b) <u>the "homogeneous system"</u>

When the liquid has been completely dispersed into froth, the viscous forces between the bubble films play an increased role, and the motion of the bubbles becomes a laminar one. The froth behaves like a liquid flowing slowly up the column and expands through the thinning of the bubble films. In the light of the results of the previous analysis. the important variables should be

h', in this case the height of froth above that height at which the homogeneous system is reached, together with D, V, S, μ. There must again be a function equal to zero,

i.e. $f(h', D, V, S, \mu) = 0$ -----------------(27)

A dimensional analysis of equation No. 27 gives

$$\phi\left(D/h',\ \frac{S}{\mu V}\right) = 0$$

Since it has been shown experimentally that in this state the height of froth is directly proportional to the rate of air flow, we have

$$\frac{\acute{h}}{D} = Q' \cdot \frac{\mu V}{S}$$

$$\therefore \quad \acute{h} = Q' \cdot \frac{D\mu}{S} \cdot V \text{-----------------------------} (28)$$

The initial dimensions of the liquid column (i.e. h_1/D) should have no longer any effect on the results of this equation, since the liquid is completely dispersed into froth. If care is taken as was stated by Bikerman, to see that the initial volume is a relatively large one, e.g. not less than 100 ccs. in apparatus No. 4 and not less than 20 ccs. in No. 5, the initial dimensions will decide only the height at which the homogeneous system is reached.

Thus Q' is another dimensionless constant which should be independent of apparatus dimensions. It is interesting to note that

$$Q' \cdot \frac{D\mu}{S} = 1/k$$

i.e. is similar to the constant of Ross's equation as already indicated on page 77 of this work.

If then the variation of froth height with flow rate is being considered for one particular solution (i.e. S constant and μ constant) we may put

$$Q' \cdot \frac{\mu}{S} = U$$

where U is a constant of dimensions, secs. cms.$^{-1}$ and equation No. 29 becomes

$$h' = U.D.\frac{R}{A} \text{ ------------------------ } (30)$$

$$\text{or } H = U.D.\frac{R}{A} + K \text{ -------------------- } (31)$$

where K is the intercept of this linear portion at zero air-flow.

Experimental.

If reference is again made to the results shown in Table XI and Figures 35 and 36, it can be seen that the linear portion of the curves for solutions of such high froth stability is relatively short. In Figure 36 only the 80% saturated solution has a linear portion long enough for accurate measurement of the gradient. The froths of the other solutions in this figure are so near their limiting height that the linear portion tends to be masked. In Figure 35 the two effects are seen better. The linear portion is quite obvious before the limiting height has its effect on the gradient. The values of U for these solutions in each apparatus have been calculated from the gradients of these linear portions and are given in Table XIII below.

In spite of the difficulties in obtaining an accurate value for the gradients, the value of U, for any solution, given by each apparatus are in good agreement indicating that U is independent of apparatus dimensions. The change in value of U with concentration of reagent is in the same sense as was Q. Since Q and U give absolute values for froth stability we may give them the term, Froth Height Stability Constants to distinguish them from the froth volume stability constant, M.

Table XIII

$$U = \frac{H_2 - H_1}{R_2 - R_1} \times \frac{A}{D}$$

Apparatus No. 4, 100 ccs. solution

A = 7.56 sq. cms. D = 3.10 cms.

Solution Strength.-	40%	50%	60%	80%
U secs. cms.^{-1}	7.57	7.70	7.38	6.89
K cms.	7.56	7.57	7.56	7.07

Apparatus No. 5, 20 ccs. solution.

A = 1.17 sq. cms. D = 1.22 cms.

Solution Strength:-	40%	50%	60%	80%
U secs. cms.^{-1}	8.41	8.79	7.91	5.96
K cms.	24.9	25.1	24.4	23.0

The Comparison of Froth Stabilities.

With the apparatus variables arbitrarily standardised attention can now be given to methods of studying the effect of reagent concentration on froth stability. The various constants, (M, Q and U) that have been derived in the foregoing work might well be employed in the comparison of froth stabilities. They would seem to have varying degrees of usefulness. Q, the square law non-dimensional constant, with its limited range of application, would serve as a measure of the stability of high stability froths since in such cases a suitable head of froth would be obtained at a low rate of air-flow. On the other hand, U, the constant of the linear law is best used for froths of low stability, because such froths, as we have already seen, have a comparatively large range of height over which the linear law is applicable.

As mentioned in the historical section of this work, previous investigators, by comparing the different methods of measuring froth stability, have shown that the total height of froth (here, H) above the porous disc in a frothing tube at dynamic equilibrium is proportional to the stability of that froth. If this statement is accepted, an anomaly is at once evident in the results of Table X when a comparison is made with Figures 35 and 36. It will be remembered that a high value of M indicated a high froth stability. Thus while Table X suggests that the solution of 80% saturation has a higher froth stability than the 60% saturated solution, Figures 35 and 36 show it to be considerable less. This would seem to indicate that M is not a true indication of stability for solutions near saturation. It is suggested that M would be most useful in comparing froth stabilities of solutions of frothing agents, where the solutions compared are those of maximum stability for the particular frothers being tested. In this way any concentration effect on M will be avoided.

Although the absolute values of stability offered by Q and U are attractive, their limited range of application will tend to make them inaccurate in many cases, and thus of little use in measuring small differences in froth stability. The fact that they are derived from gradient measurements makes them less sensitive than a single determination of froth height. For example in the linear portions of the curves in Figures 35, 36, and 37 the gradients of the 40% and 50% saturated solutions are nearly equal while at some rates of flow (e.g. in apparatus No. 4 above 8.0 ccs./sec. and in apparatus No. 5 above 1.0 ccs./sec.) there is as much as 0.8 cms. difference in height between them. This is quite a large difference when froth heights can be measured to - 0.02 cms. The difference in froth height is roughly proportional to the rate of air flow used. Thus where comparative values of froth stability are required froth height measurements at a fixed rate of air flow are more sensitive and can be made more quickly than determinations of M, Q, or U. The change in sensitivity, i.e. the variation of froth height with concentration of reagent at a number of different air flow rates, is obvious from Figure 39. As the rate of air flow is increased, the maximum of the plot of froth height against reagent concentration can be seen to develop from a small rise to a sharp peak. The position of this peak with reference to the concentration axis seems to be unaffected by rate of air flow. By making measurements, therefore, at a suitable air flow rate the sensitivity of the experiment can be set at the value required.

For these reasons, Q and U will not be used in the experiments which follow, but froth heights will be measured at arbitrary rates of air flow. Where absolute values of froth stability are required M will be calculated, but care will be taken to see that M is used only for the comparison of solutions whose stabilities lie at similar points on their respective froth stability/concentration curves, i.e. at the maxima.

The Variation of Froth Stability with Concentration of Frother.

In the measurement of comparative froth stabilities by the bubble column the determination of total height of froth above the porous diaphragm at dynamic equilibrium is the simplest and quickest method, and, as shown above, the order of sensitivity of the method is controlled by the rate of air-flow. It is thus very suitable for plotting the position of maximum froth stability from solutions covering a range of reagent concentration. Of course, using this method, the solutions compared must have the same initial volume, be at the same temperature, be subjected to the same rate of air flow, and be compared in the same apparatus.

Many investigators have indicated that solutions of surface active agents show a maximum froth stability at some definite concentration value. Bartsch determined this value for a large number of substances, but his results suffered from the crudity of the agitation method he used.

The surface active agents, or frothers, chosen for this investigation were as in the previous experiments the lower monohydric alcohols as being the simplest type available.

Apparatus.

Froth apparatus Nos. 3 and 4 were used in this investigation. No. 3 was used first for the alcohols of low froth stability but it soon became obvious that the frothing tube (50 cms.) would be dangerously short for the froths produced by the higher alcohols with the initial volume of solution being used. Thus frothing apparatus No. 4 (see figure 21) was brought into use, with its 100 cm. frothing tube. In changing from No. 3 to No. 4 a test was carried out to ascertain if a correction factor would be necessary for comparing the results obtained from the two apparatus, but the difference in froth height for the same solution was not great enough (never more than 0.5 cm. difference in 40 cms.) to warrant a correction factor. This may be attributed to the fact that the apparatus had been made as far as possible dimensionally identical and had porous discs of similar porosity (40-50 microns.) Rate of flow measurement was by an orifice type flowmeter which had been previously calibrated by a wet gasmeter. In all the tests water was circulated through the thermostatic jacket to keep the solutions at 25°C ± 0.2°C. The automatic pipettes described previously were used for transfer of solutions. A dust-cap made from a small beaker inverted and filled with cotton wool was used on top of the frothing tube during tests.

Purification of Reagents and Preparation of Solutions.

The alcohols were obtained from different sources and were of different degrees of purity.

Methanol and Ethanol were the absolute alcohols available in the laboratory. They were dried by refluxing over Grignard Magnesium, the methanol for 24 hours, the ethanol for 48 hours. The samples were then redistilled. The densities of the dried materials were taken as a check on their purity. The values given below are compared with those from the National Critical Tables.

Density of dried methanol at 20°C = 0.7921 gm./cc.
Density of 100% methanol (I.C.T.) at 20°C = 0.7917 "
Density of dried ethanol at 20°C = 0.7894 "
Density of 100% ethanol (I.C.T.) at 20°C = 0.78934 "

Samples of the alcohols, n-propanol, isopropanol, n-butanol, iso-butanol, sec. butanol were obtained pure from B.D.H. These were in carefully sealed bottles and therefore it was taken that their only impurity likely to effect results would be water. Density determinations were made on the samples.

Density of B.D.H. n-propyl alcohol at 25°C = 0.7999 gm./cc.
Density of 100% n-propyl alcohol at 25°C (I.C.T.) = 0.8001 "
Density of B.D.H. isopropyl alcohol at 20°C = 0.7875 "
Density of 100% isopropanol at 20°C (I.C.T.) = 0.7854 "
Density of 99% isopropanol at 20°C (I.C.T.) = 0.7877 "

Density of B.D.H. n-butyl alcohol at 20°C = 0.8110 "
Density of 100% n-butanol at 20°C (I.C.T.) = 0.8097 "

Density of B.D.H. isobutyl alcohol at 20°C = 0.8041 "
Density of 100% isobutanol at 20°C (I.C.T.) = 0.8017 "

Density of B.D.H. sec. butyl alcohol at 20°C = 0.8039 "
Density of sec. butanol at 20°C (Handbk. Chem. and Physics.) = 0.808 "
(This was the only figure available for this alcohol)

The Tert. Butanol obtained was a commercial sample and was therefore distilled through a Fenske fractionating column. The fraction distilling between 82.0°C and 82.5°C was collected. (B.P. of pure Tert. Butanol = 82.5°C)

Density of redistilled tert. butanol at 30°C = 0.7787gm./cc

Density of tert. butanol at 30°C (Dict. App. Chem. Thorpe.) = 0.7788 "

The n-amyl alcohol was B.D.H. pure.

Density of B.D.H. n-amyl alcohol at 20°C = 0.8144 "

Density of 100% n-amyl alcohol at 20°C (Addison, J.C.S., p.98, 1945.) = 0.8139 "

The sample of iso-amyl alcohol obtained was of unknown origin and was therefore also carefully redistilled, the fraction distilling between 130.5°C and 131.5°C being collected. (B.P. of pure iso-amyl alcohol = 131.5°C.)

Density of redistilled iso-amyl alcohol at 20°C = 0.8128 "

Density of iso-amyl alcohol at 20°C (Addison, J.C.S., p.98, 1945). = 0.8127 "

The heptyl alcohols were B.D.H. pure.

Density of B.D.H. n-heptyl alcohol at 20°C = 0.8212 "

Density of n-Heptanol at 20°C (Handbk. Chem. and Physics.) = 0.8219 "

Density of B.D.H. sec-heptyl alcohol at 20°C (i.e. 4-heptanol) = 0.8183 "

Density of 4-heptanol at 20°C (Handbk. Chem. and Physics.) = 0.8185 "

Solutions of the above alcohols were prepared on a w/w percentage basis in water double distilled and condensed on Pyrex glass. The weight of alcohol required for a solution was calculated and accurately weighed out using micro-pipettes. This amount was then made up to the required volume with water and stored in carefully cleaned glass stoppered bottles. In the case of heptyl alcohols, aqueous solutions were prepared by suitably diluting a saturated solution. This was prepared by shaking excess alcohol in distilled water for 48 hours at 25°C. For n-Heptanol the concentration in the saturated solution was taken to be that given by Butler (44), viz. 0.180 gms. per 100 gms. saturated solution at 25°C. No figure could be found for the solubility of the secondary heptyl alcohol, 4-Heptanol. Stress must be laid here on the absolute cleanliness of all apparatus necessary in this work. Chromic acid was used freely to remove grease films from all glassware. Solutions were used as soon as possible after being prepared, but later tests showed that many stored for over a month under these conditions showed no change in froth stability.

Frothing Tests.

The first tests made were with solutions of ethanol. The whole range (0-100% ethanol) was covered to verify the general shape of the curve indicated by previous workers for solutions of a surface active agent in water. For the other alcohols only a suitable range of concentration values to show the position of maximum froth stability were tested.

The frothing tube was first thoroughly cleaned with chromic acid followed by double distilled water. The dust cap was always placed on the top of the column during the interval of drawing the washings to waste through the porous disc. The tube was finally rinsed out with a little of the solution to be frothed and that drawn to waste too. It was found better to have a small rate of air flow passing into the tube even when it was under the slight vacuum of the waste pump. This made doubly sure that no waste liquid traversed the loop and entered the air line. The vacuum line was then closed, the air flow brought up to a suitable value and the volume of solution to be tested transferred to the tube by means of the automatic pipette.

For the earlier alcohols two volumes of each solution (50 ccs. and 100 ccs.) were tested from separate pipettes. This was done to prevent the accidental contamination of one pipette passing unnoticed, and to allow us to fall back on the froth height for 50 ccs. if the 100 cc. value for later alcohols could not be maintained in the apparatus. Since this was found unnecessary the use of the 50 cc. pipette was finally discontinued.

As a check on local contamination of the tube each solution was frothed at three rates of flow, giving flowmeter readings as shown in Table XIV below:-

Table /

Table XIV.

Abritrary Air Flow Rates for Frothing Apparatus No. 4.

Flow meter Reading (cm. water)		Rate of Flow at Flowmeter (15°C)		Rate of Flow at Sintered disc (25°C)	
		cu.ft/hr.	litres/hr.	cu.ft./hr	litres/hr.
Rate No. 1	2.0	1.39	39.4	1.44	40.8
Rate No.2	4.0	2.05	58.0	2.12	60.0
Rate No.3	6.0	2.62	74.2	2.71	76.8

There was a chance that variation of room temperature might cause variation of volume flow at the porous disc, so care was taken to carry out the tests during that part of the day when room temperature was 15°C ± 2.0°C. The three rates of flow allowed three curves to be plotted for the one solution in the concentration range covered and showed up any inconsistency in any one of the curves. It has already been shown that the variation of froth height with concentration of frother is proportional to the rate of air flow, thus the highest rate of flow was the most suitable for showing the position of the maximum, but, of course, the errors involved were also at their highest. On the other hand the lower rate of flow values were less subject to error and the maximum was flatter. Thus one could obtain the correct shape of the 6 cm. curve from the lower flow rate curves and the exact position of the maximum from the 6 cm. curve itself.

The solution under test was gently frothed for five minutes to bring it to the temperature of its surroundings. The rate of flow was then lowered to break the froth and raised to the highest rate of flow value. When dynamic equilibrium was reached the froth height was measured, then the froth was broken and built up again in a repeat test. This was done in turn with each of the air flow values. Finally, the solution was drawn to waste and a new sample substituted.

Results.

Of the alcohols tested the results for methanol were the most difficult to obtain due to its low froth stability and flattish maximum. The results for the individual alcohols are plotted in Figs. 38-50 respectively. Difficulty was also experienced with the heptyl alcohols. Under the conditions of the experiment the rate of air flow associated with the limiting height of froth was, for most of the heptyl alcohol solutions, below the 6 cms. rate and even in some cases below 4 cms. Solutions of these strongly surface active substances particularly near saturation have such small-bubbled froths that complete dispersion is achieved at a comparatively low rate of air flow. Froth heights cannot be measured above the limiting height since the column no longer expands but is oscillating violently as large bubbles pass up through it. These large bubbles tend to destroy the column, as shown in Figure 48 where the froth height of the 100%

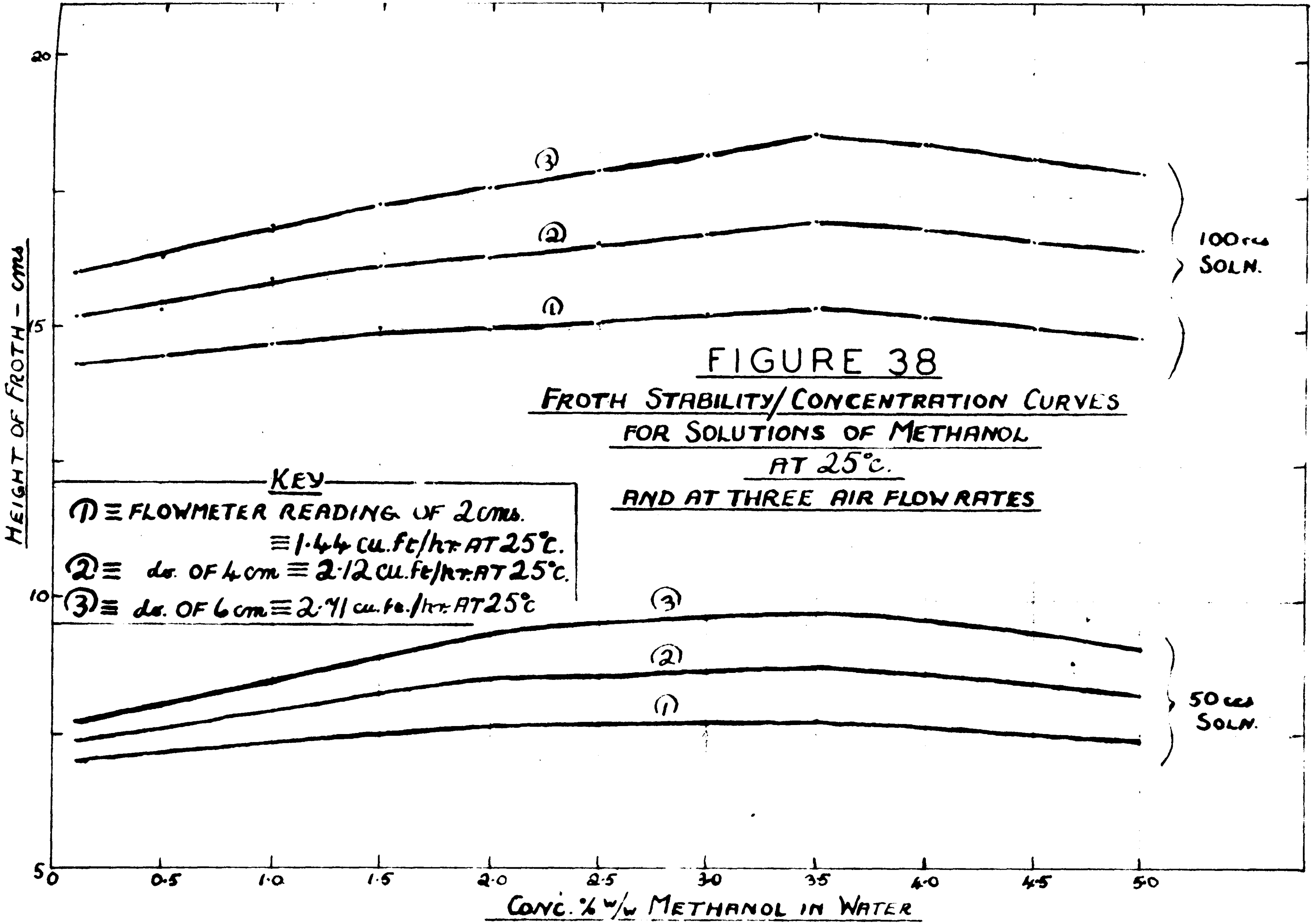


FIGURE 38

FROTH STABILITY/CONCENTRATION CURVES FOR SOLUTIONS OF METHANOL AT 25°C. AND AT THREE AIR FLOW RATES

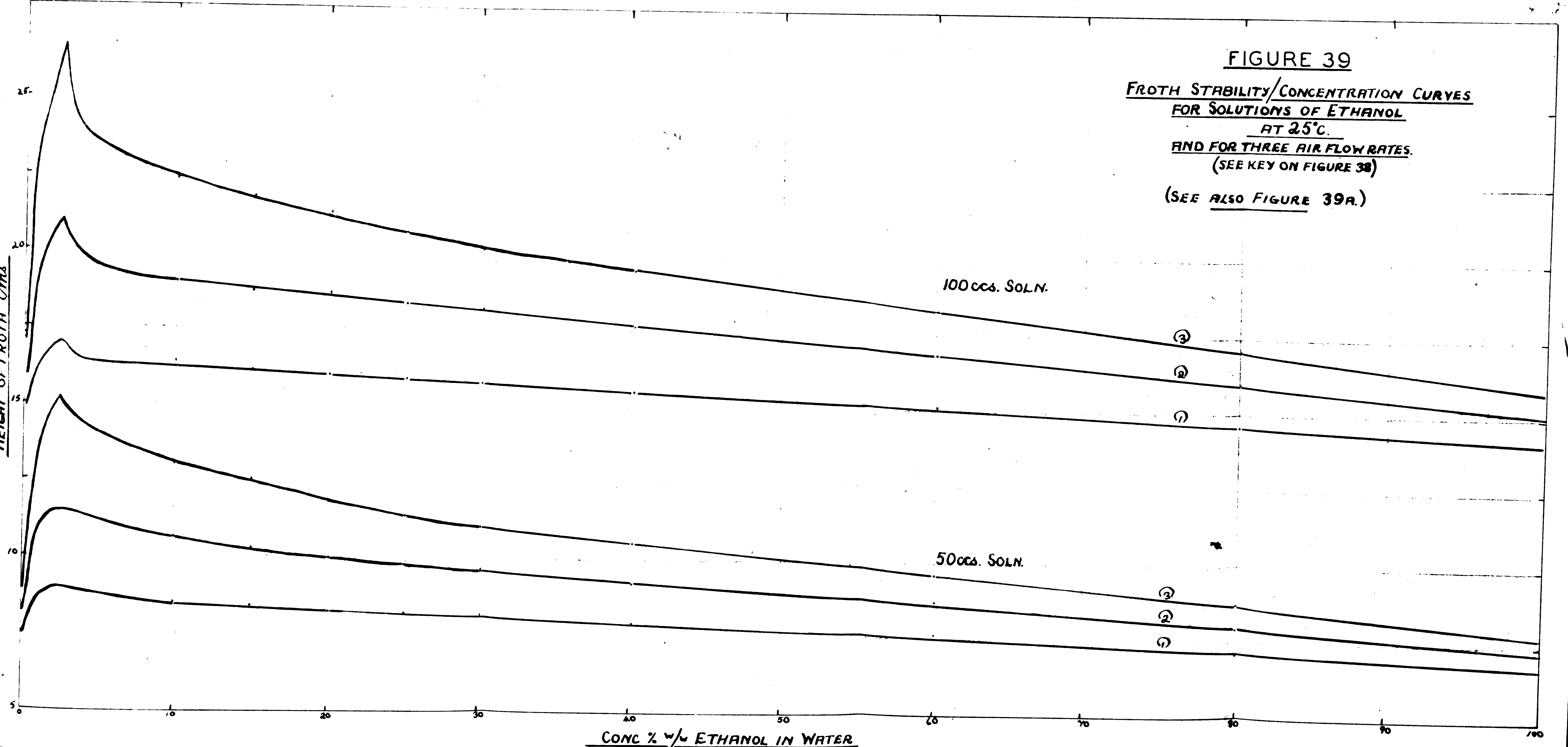


FIGURE 39

FROTH STABILITY/CONCENTRATION CURVES FOR SOLUTIONS OF ETHANOL AT 25°C. AND FOR THREE AIR FLOW RATES. (SEE KEY ON FIGURE 38)

(SEE ALSO FIGURE 39A.)

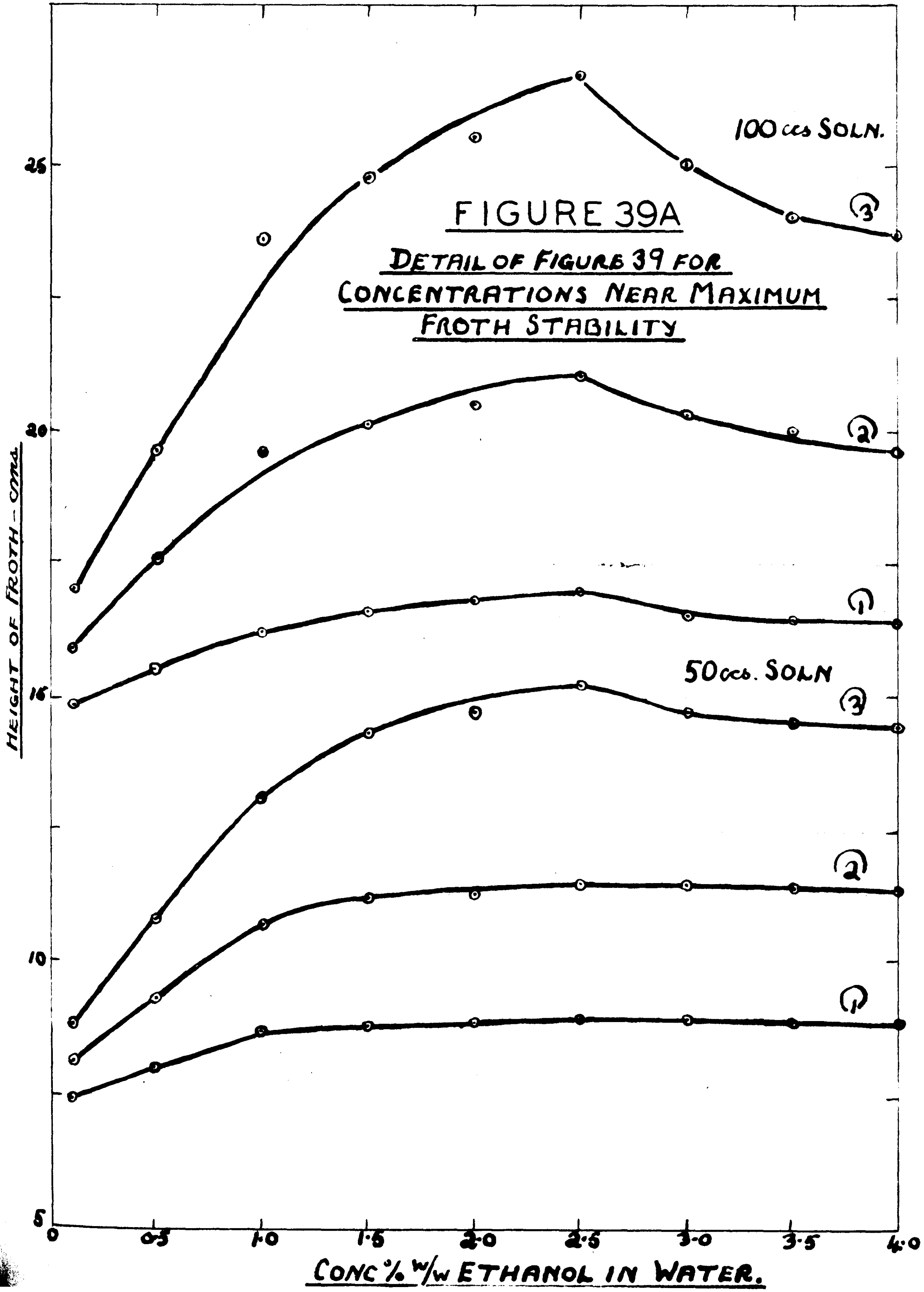


FIGURE 39A

DETAIL OF FIGURE 39 FOR CONCENTRATIONS NEAR MAXIMUM FROTH STABILITY

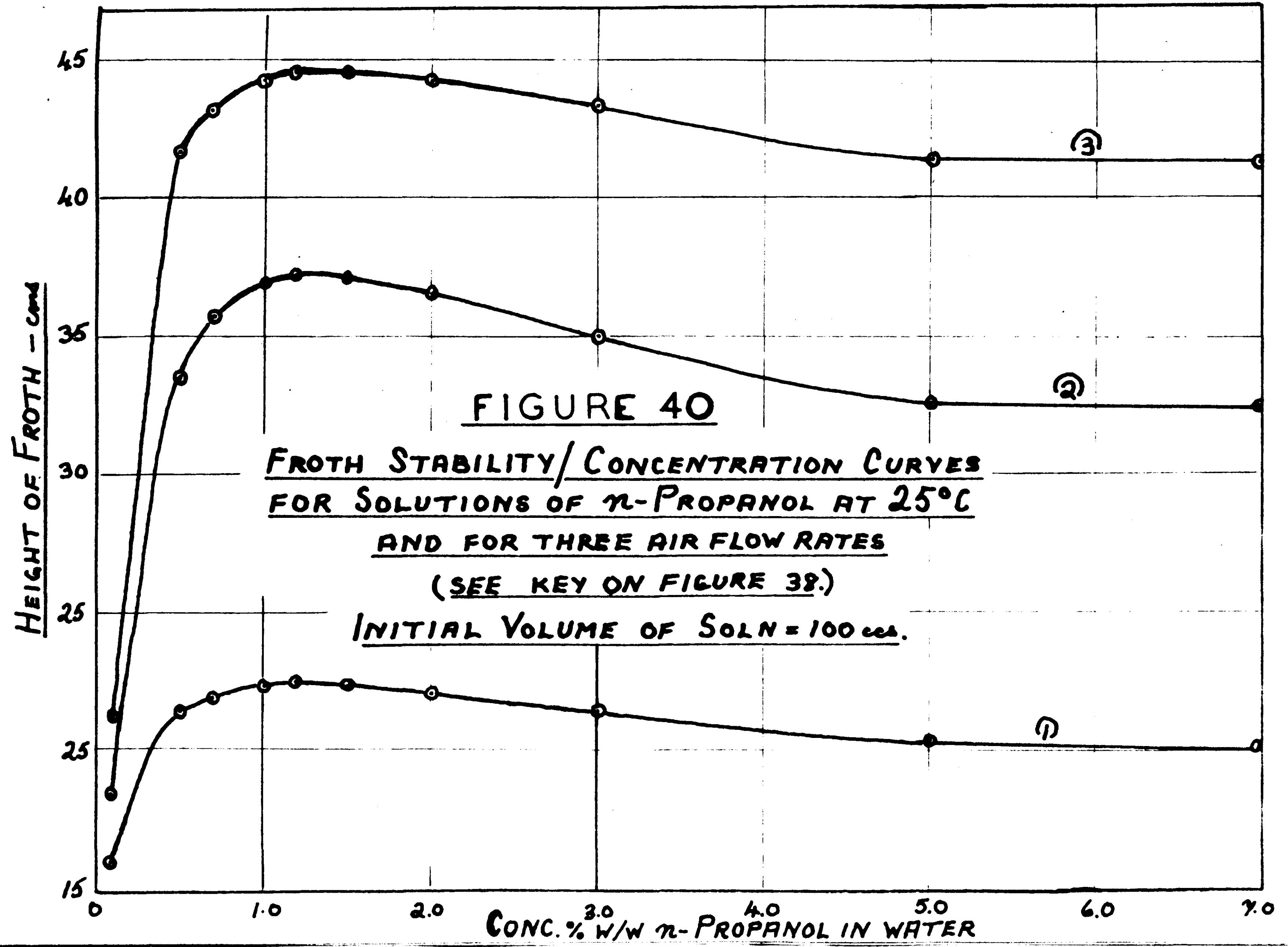


FIGURE 40

FROTH STABILITY/CONCENTRATION CURVES FOR SOLUTIONS OF n-PROPANOL AT 25°C AND FOR THREE AIR FLOW RATES

(SEE KEY ON FIGURE 38.)

INITIAL VOLUME OF SOLN = 100 ccs.

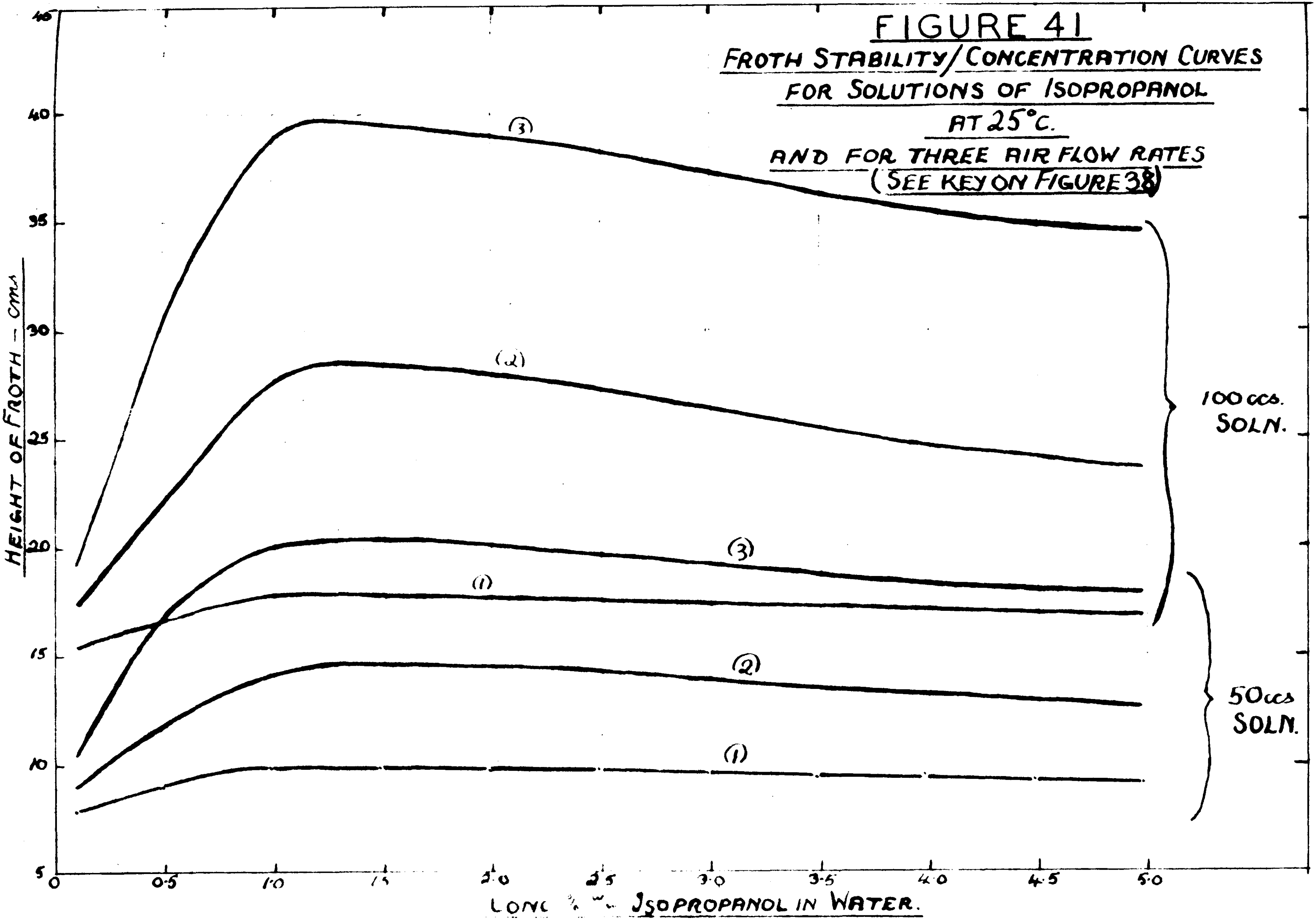


FIGURE 41

FROTH STABILITY/CONCENTRATION CURVES FOR SOLUTIONS OF ISOPROPANOL AT 25°C. AND FOR THREE AIR FLOW RATES (SEE KEY ON FIGURE 38)

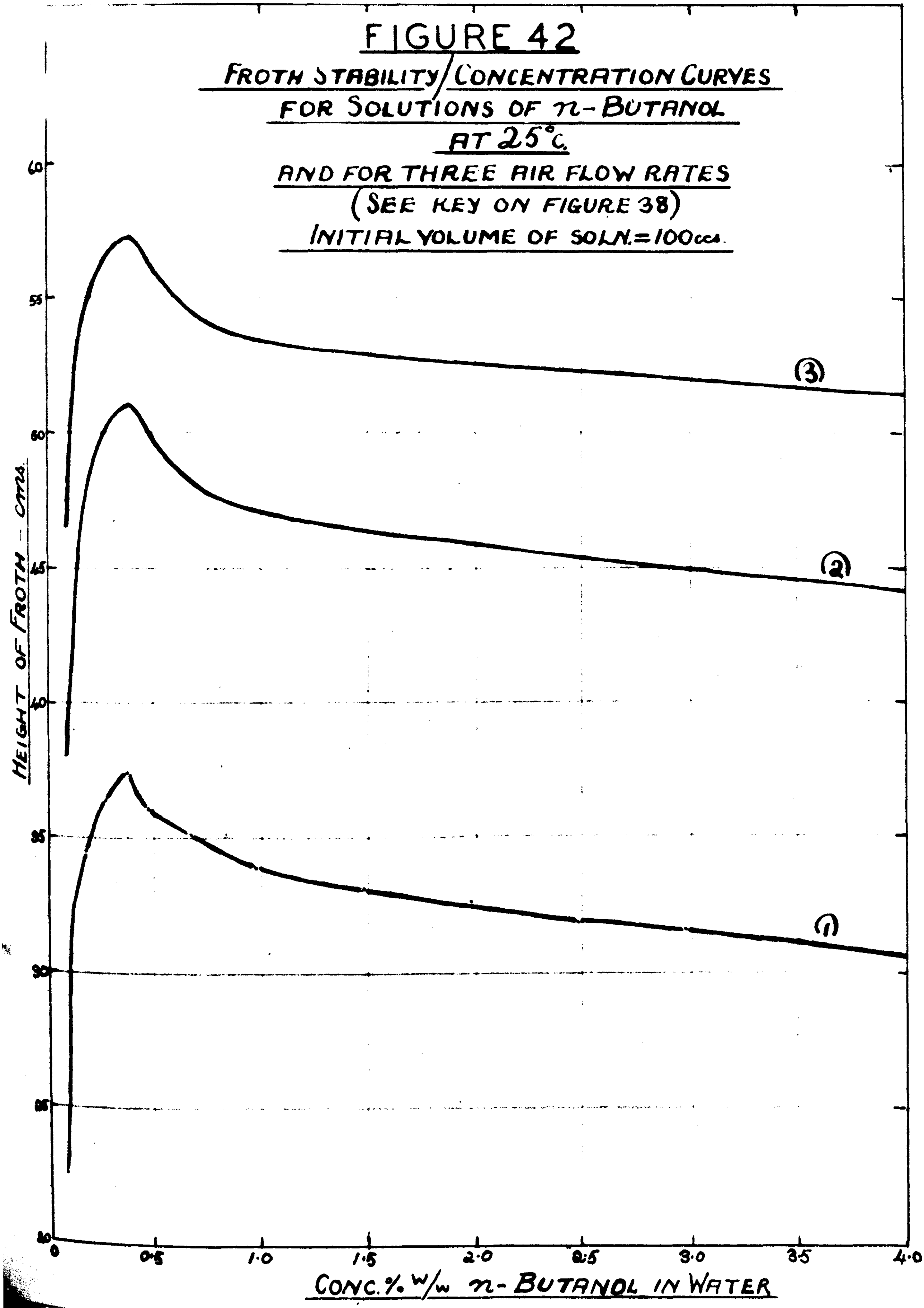


FIGURE 42

FROTH STABILITY/CONCENTRATION CURVES
FOR SOLUTIONS OF n-BUTANOL
AT 25°C.
AND FOR THREE AIR FLOW RATES
(SEE KEY ON FIGURE 38)
INITIAL VOLUME OF SOLN.=100ccs.

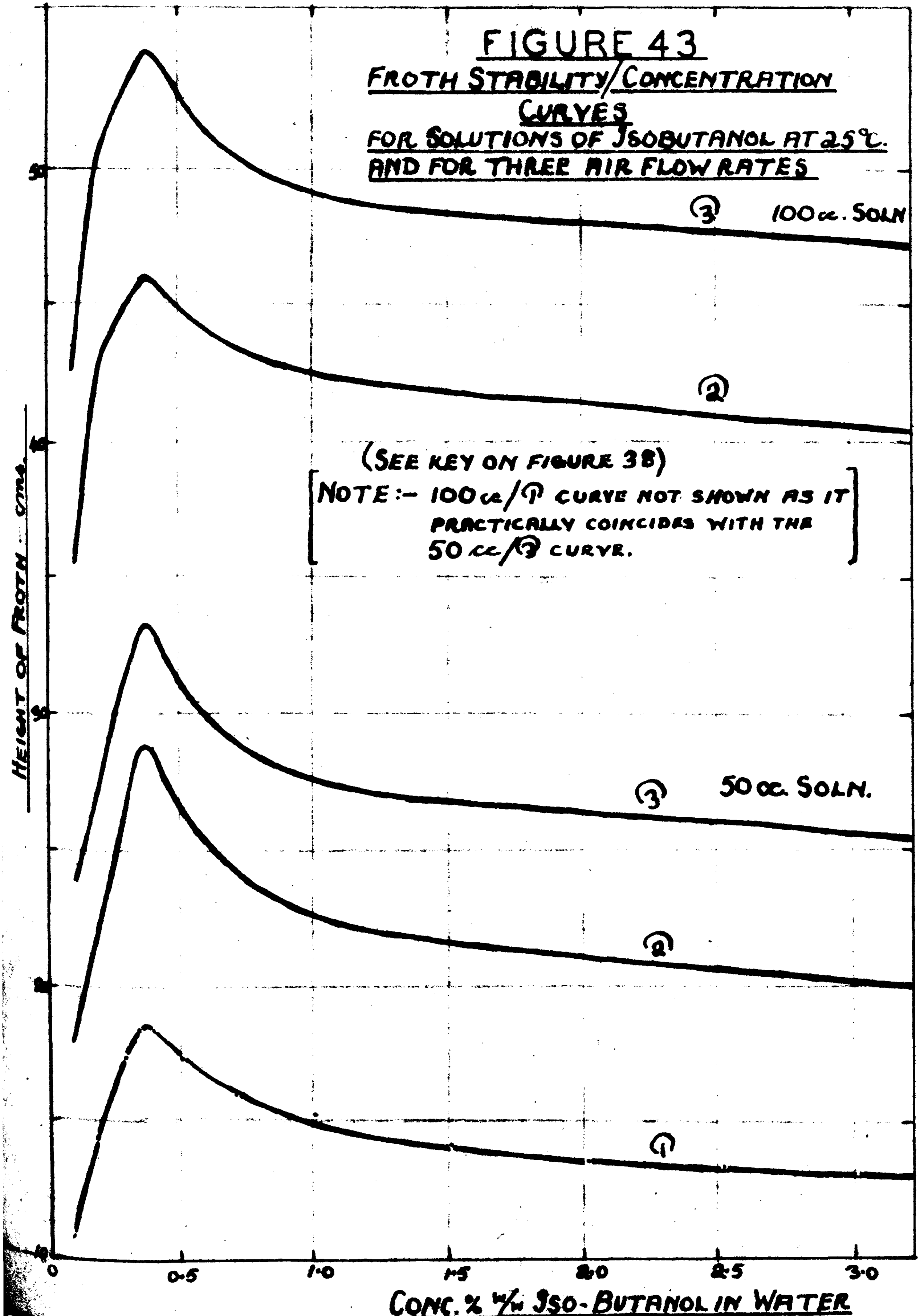


FIGURE 43

FROTH STABILITY/CONCENTRATION CURVES

FOR SOLUTIONS OF ISOBUTANOL AT 25°C. AND FOR THREE AIR FLOW RATES

(SEE KEY ON FIGURE 38)

[NOTE:- 100cc/① CURVE NOT SHOWN AS IT PRACTICALLY COINCIDES WITH THE 50cc/③ CURVE.]

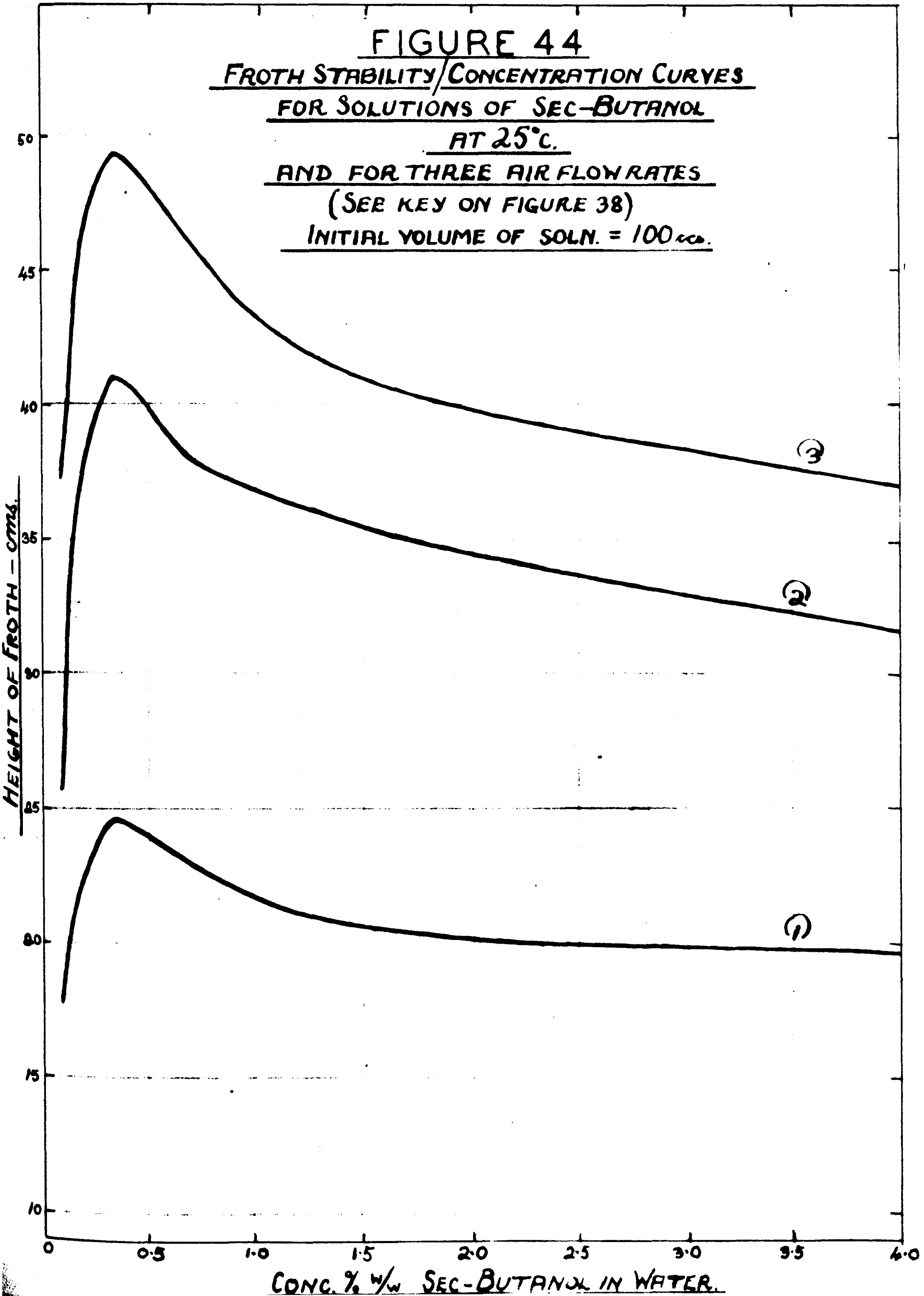


FIGURE 44

FROTH STABILITY/CONCENTRATION CURVES FOR SOLUTIONS OF SEC-BUTANOL AT 25°C. AND FOR THREE AIR FLOW RATES (SEE KEY ON FIGURE 38)

INITIAL VOLUME OF SOLN. = 100 ccs.

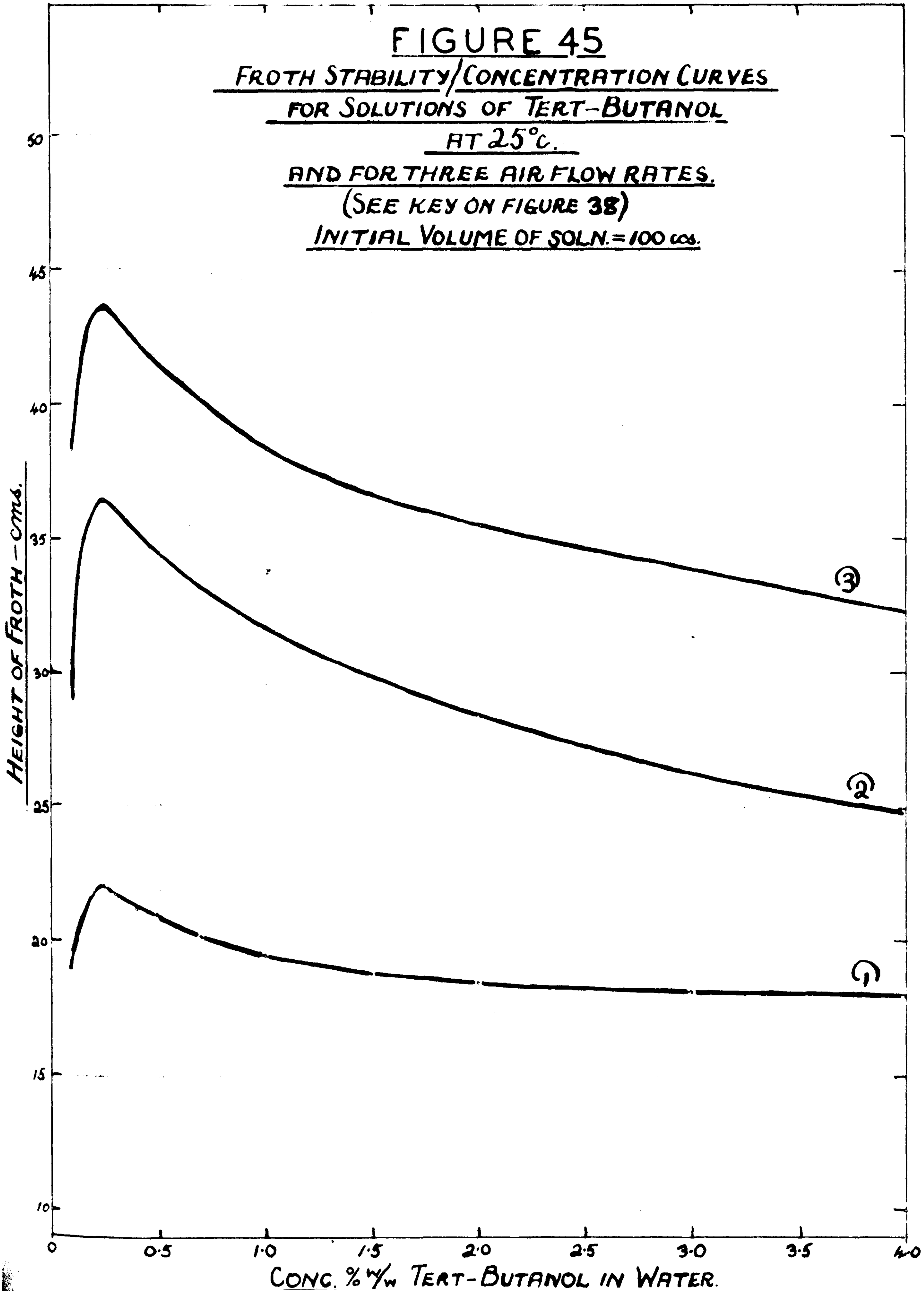


FIGURE 45

FROTH STABILITY/CONCENTRATION CURVES
FOR SOLUTIONS OF TERT-BUTANOL
AT 25°C.
AND FOR THREE AIR FLOW RATES.
(SEE KEY ON FIGURE 38)
INITIAL VOLUME OF SOLN. = 100 ccs.

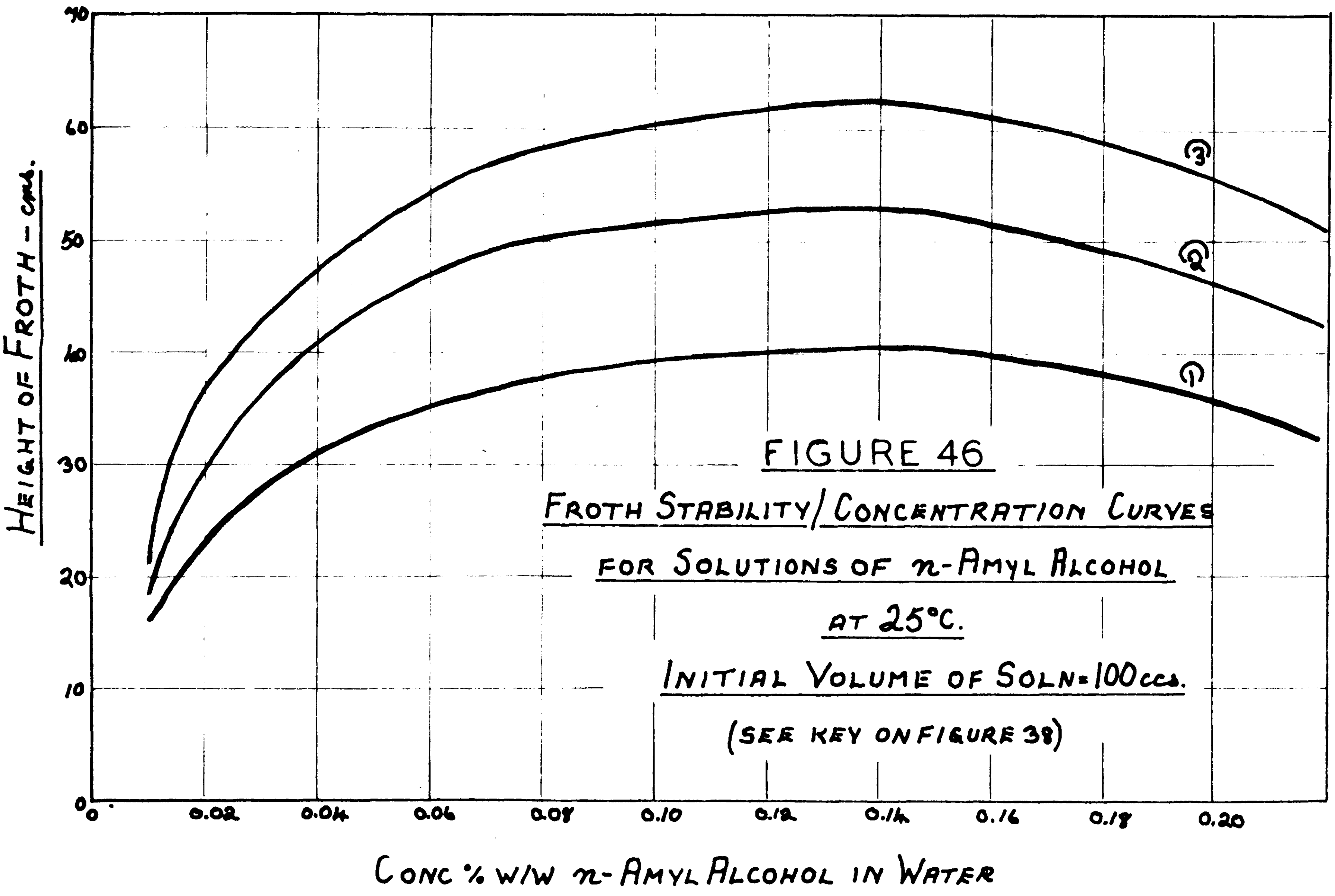


FIGURE 46

FROTH STABILITY/CONCENTRATION CURVES FOR SOLUTIONS OF n-AMYL ALCOHOL AT 25°C.

INITIAL VOLUME OF SOLN = 100 ccs.

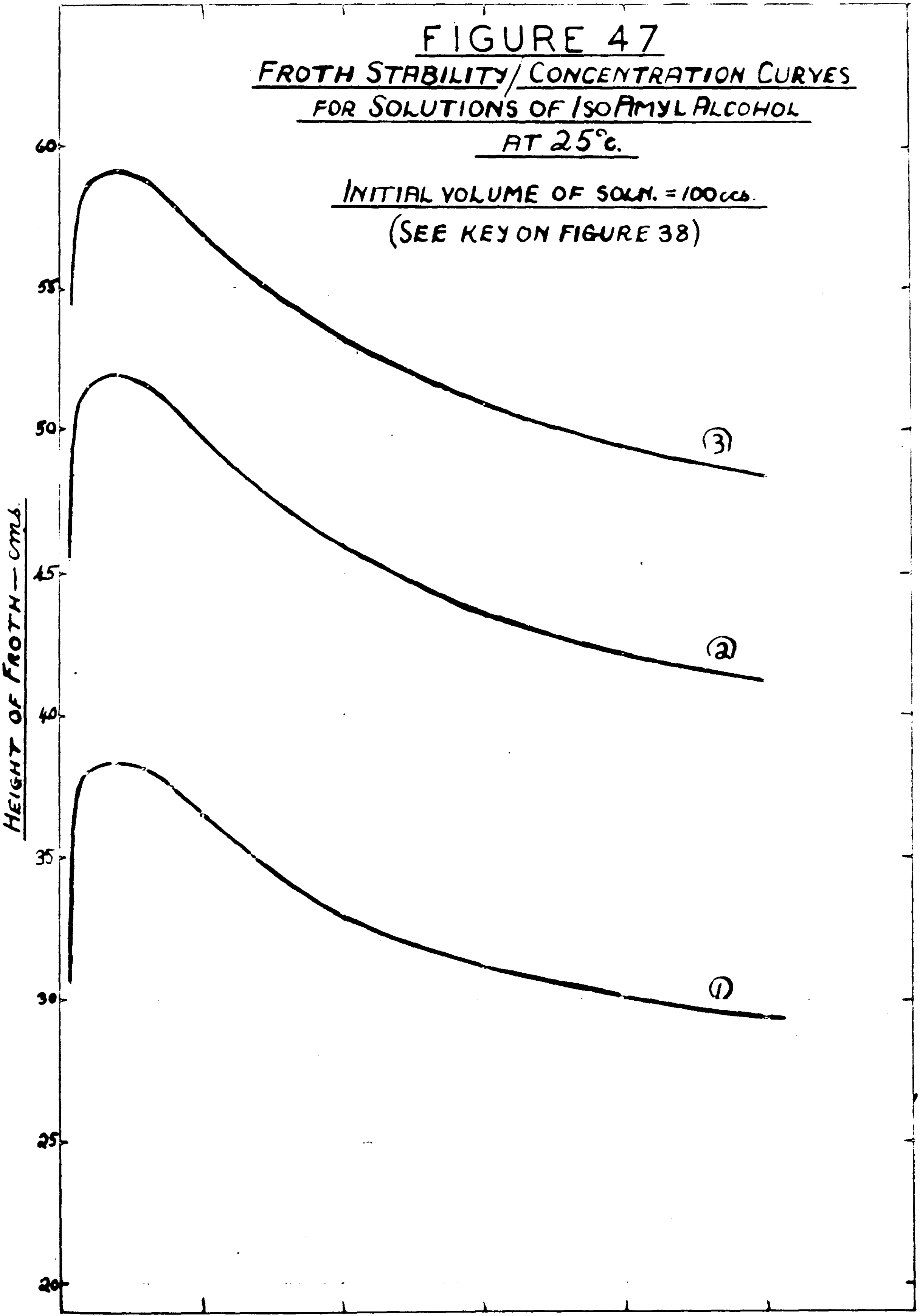
(SEE KEY ON FIGURE 38)

FIGURE 47

FROTH STABILITY/CONCENTRATION CURVES FOR SOLUTIONS OF ISO AMYL ALCOHOL AT 25°C.

INITIAL VOLUME OF SOLN. = 100 ccs.

(SEE KEY ON FIGURE 38)



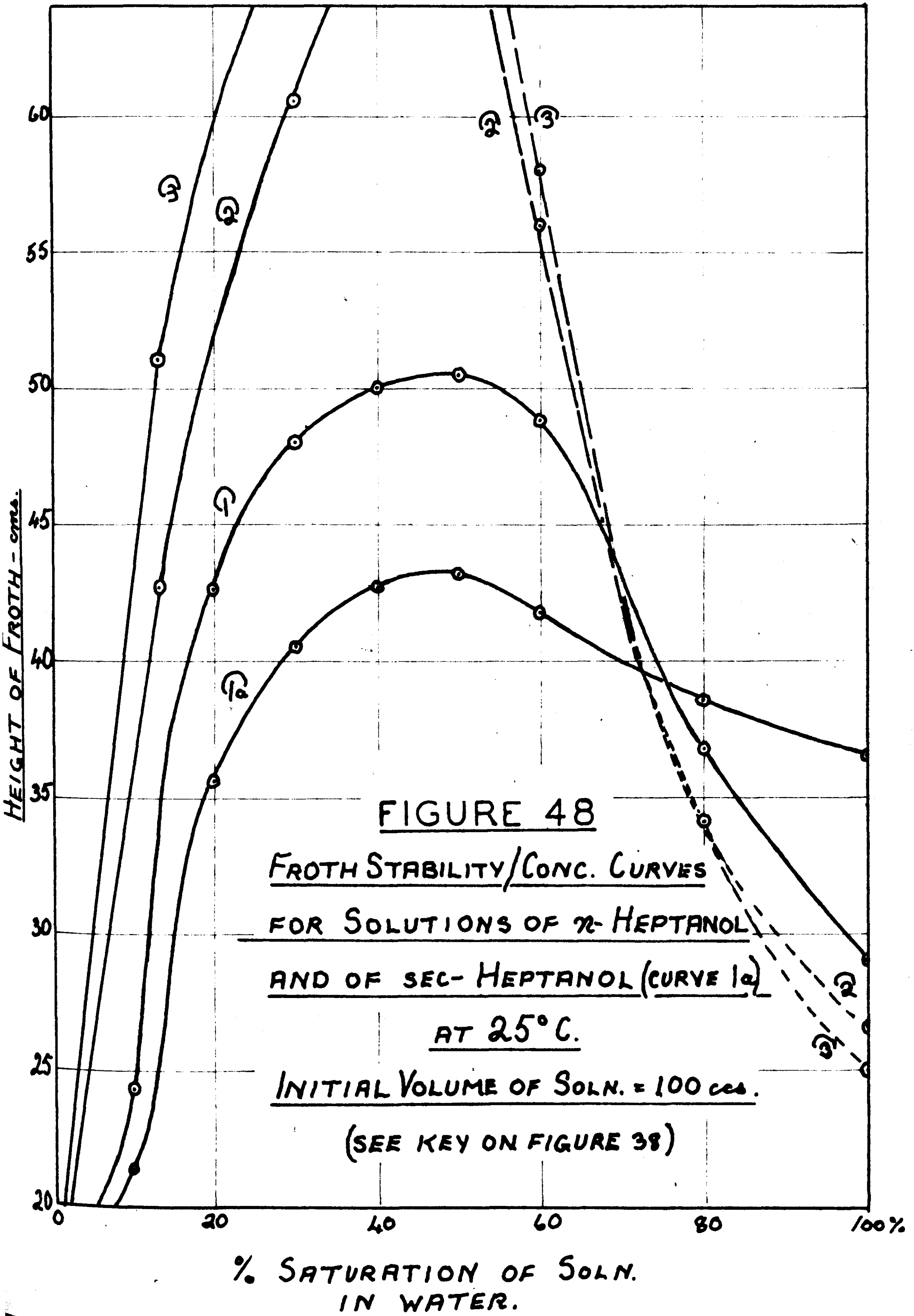


FIGURE 48

FROTH STABILITY/CONC. CURVES FOR SOLUTIONS OF n-HEPTANOL AND OF SEC-HEPTANOL (CURVE 1a) AT 25°C.

INITIAL VOLUME OF SOLN. = 100 ccs.

(SEE KEY ON FIGURE 38)

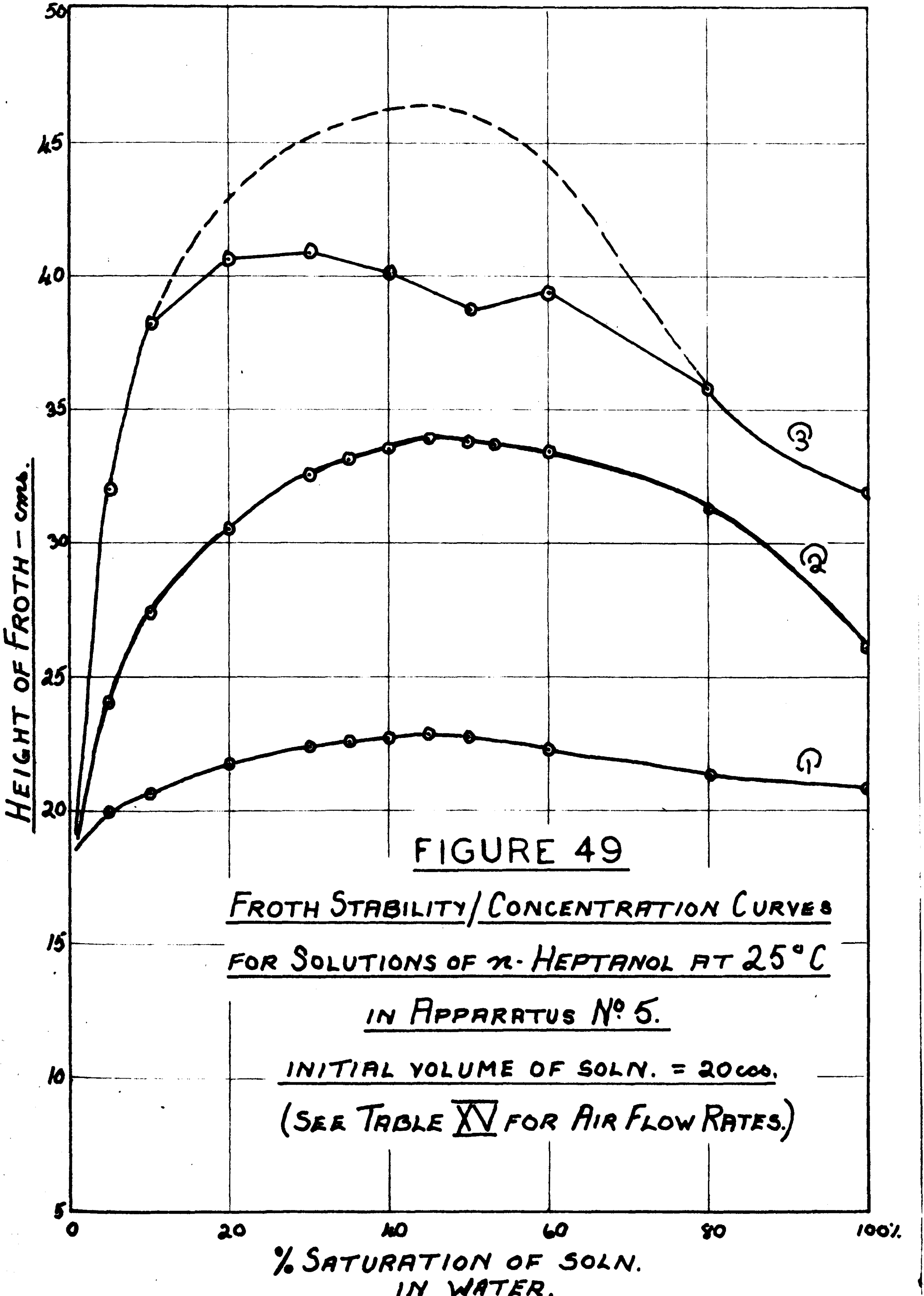


FIGURE 49

FROTH STABILITY/CONCENTRATION CURVES FOR SOLUTIONS OF n-HEPTANOL AT 25°C IN APPARATUS No. 5.

INITIAL VOLUME OF SOLN. = 20ccs.

(SEE TABLE XV FOR AIR FLOW RATES.)

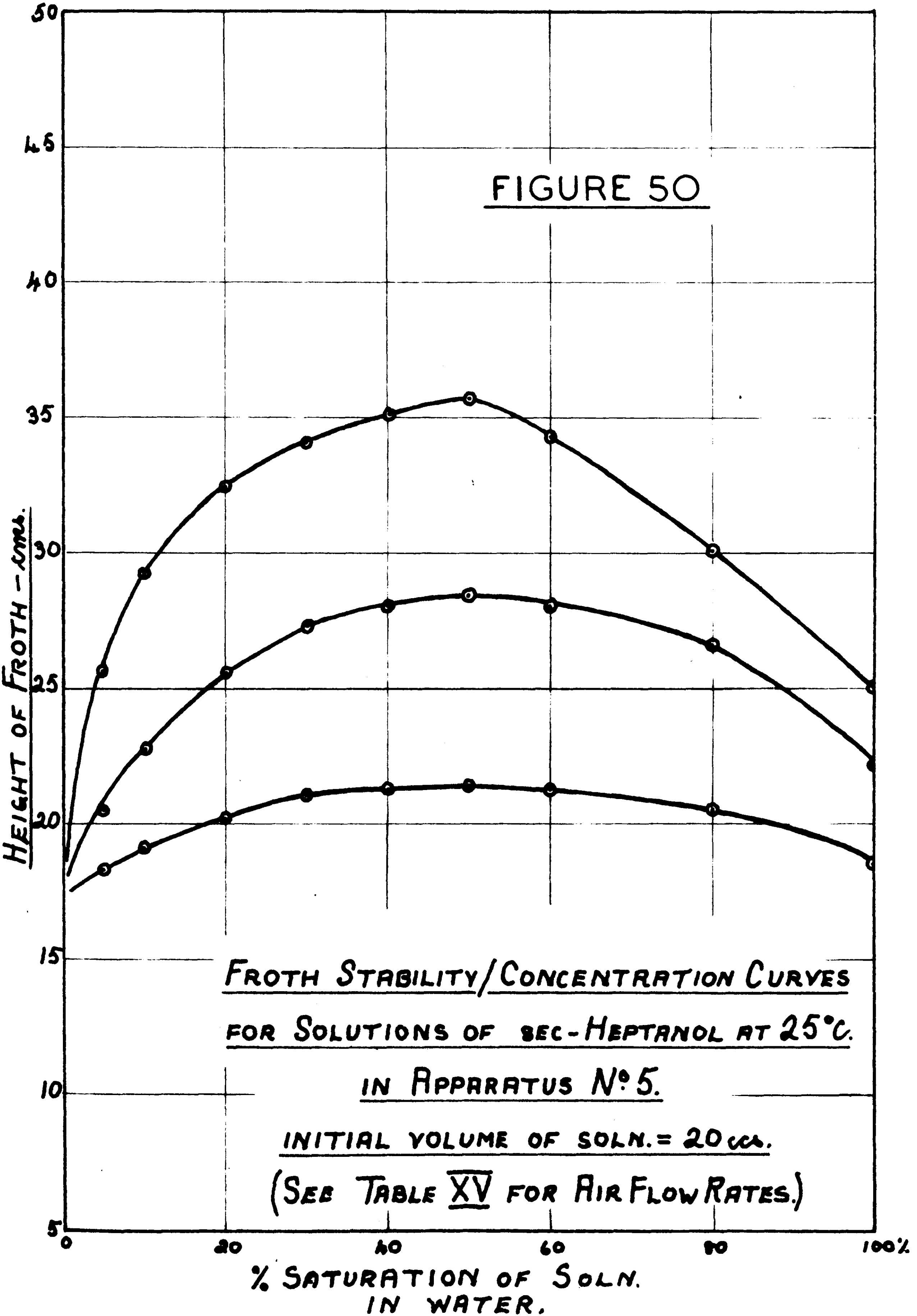


FIGURE 50

FROTH STABILITY/CONCENTRATION CURVES
FOR SOLUTIONS OF SEC-HEPTANOL AT 25°C.
IN APPARATUS Nº 5.

INITIAL VOLUME OF SOLN. = 20 ccs.

(SEE TABLE XV FOR AIR FLOW RATES.)

saturated solution of n-heptanol at the 6 cm. air flow is lower than at the 4 cm. air flow. No accurate heights could be obtained for these solutions at the 4 cm. or 6 cm. rates. The curves plotted at the 2 cm. flow rate, however, for solutions of the two heptanols are compared in Figure 48. The fragments of the 4 cm. and 6 cm. curves for n-heptanol solutions are also shown.

The heptanol solutions were then tested in apparatus No. 5 using an initial volume of 20 ccs. Three arbitrary air flow rates were chosen as indicated in Table XV below and the results are plotted in Figures 49 and 50.

Table XV.

Arbitrary Air Flow Rates for Frothing Apparatus No. 5.

	Flowmeter Reading (cms. water)	Rate of Flow at Flowmeter (15°C.)	Rate of flow at sintered disc. (25°C.)
Rate 1.	2.0	1.42 litres/hr.	1.46 litres/hr.
Rate 2.	4.0	2.73 "	2.86 "
Rate 3.	6.0	4.07 "	4.19 "

For all the secondary heptanol solutions the rate of air flow associated with the limiting height was now above the highest of the three rates chosen, but for most of the n-heptanol solutions the highest of the three rates was again above the limit. This is shown by the erratic shape of the topmost full-line curve of Figure 49. The broken-line curve indicates the probable shape of the topmost curve were there sufficient liquid in the tube to allow further froth to be formed.

Measurements on the 100% saturated solutions had to be made quickly since continued frothing caused precipitation of droplets of alcohol in the froth. The sudden changes of surface area taking place at the top of the froth were causing the concentration of adsorbed molecules to locally exceed the saturation value. The resultant decrease in bulk concentration of alcohol caused a progressive increase in the height of the froth produced by the solution.

The 6 cm. curve for all the alcohols except the heptanols are compared in Figure 51. Their significance is discussed later. At this point it was important to see the effect of temperature on the position of the froth stability maximum with reference to the concentration axis, before one could attach any significance to the values obtained above.

Effect of Temperature on the concentration value at which maximum froth stability occurs.

Isopropanol was chosen as the alcohol to be tested and frothing was carried out as explained above. 100 ccs. of solution were taken in every case. The concentration range was covered for solution temperatures of 25°; 35°; 45° and 60°C. A temperature correction was applied to the flowmeter to offset its difference in temperature from the temperature of the solution and thus correct changes in volume flow.

The results of the test are shown plotted on Figure 52 and it can be seen that there is a slight movement of the

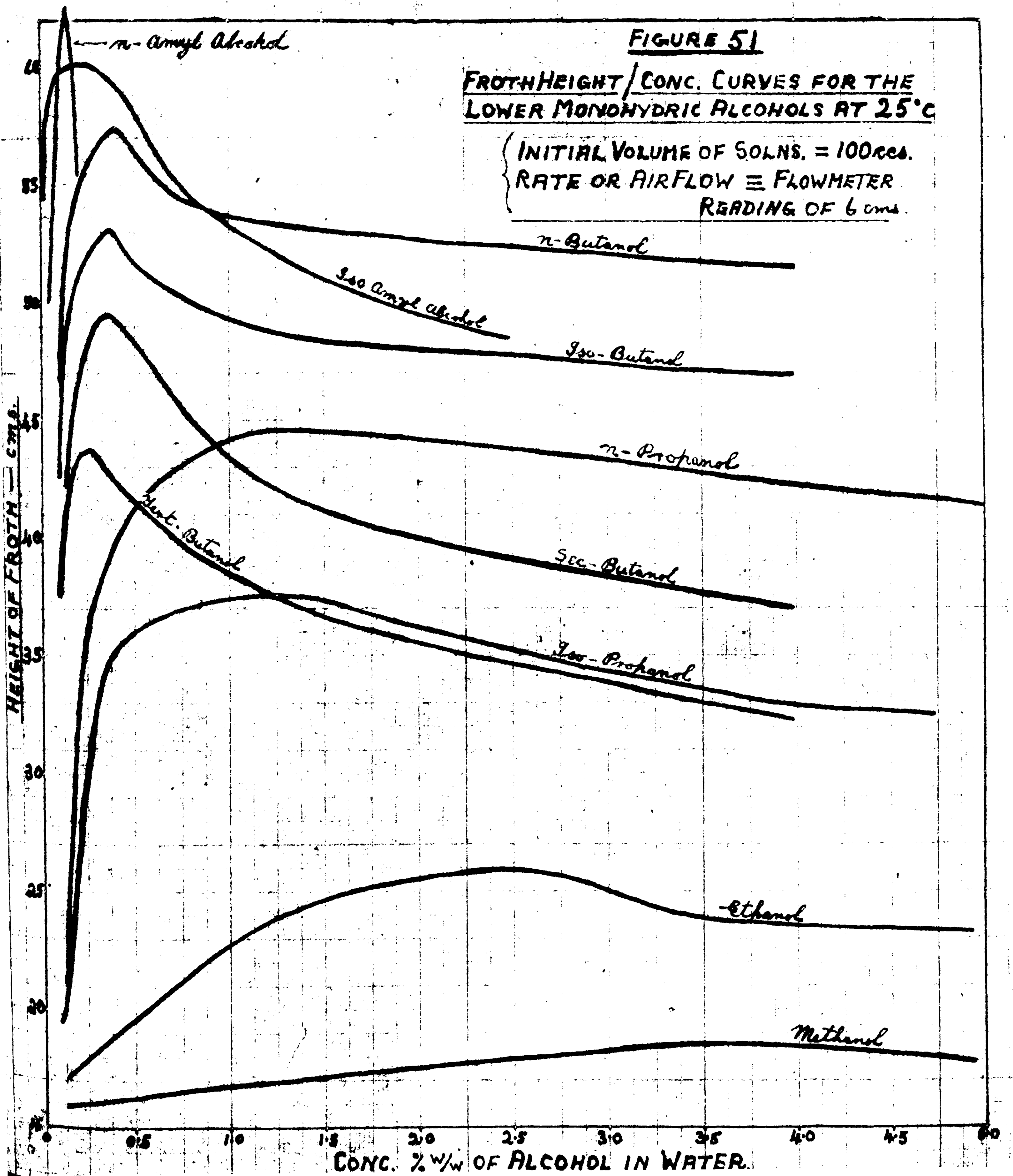


FIGURE 51

FROTH HEIGHT / CONC. CURVES FOR THE LOWER MONOHYDRIC ALCOHOLS AT 25°C

INITIAL VOLUME OF SOLNS. = 100 ccs.
RATE OF AIRFLOW ≡ FLOWMETER READING OF 6 cms.

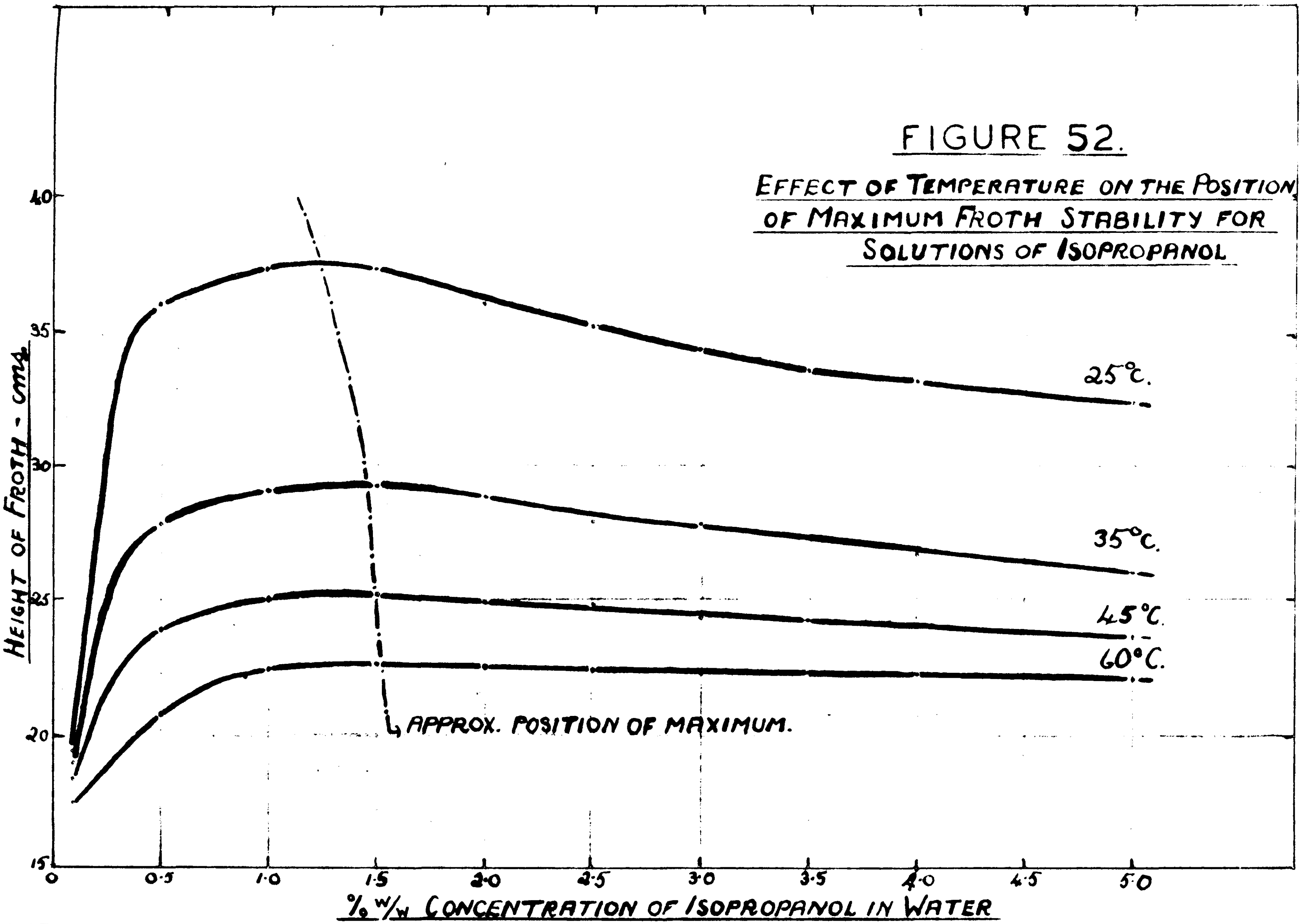


FIGURE 52.

EFFECT OF TEMPERATURE ON THE POSITION OF MAXIMUM FROTH STABILITY FOR SOLUTIONS OF ISOPROPANOL maximum value with temperature change. But considering the large range of temperature covered (35°C) we may say that the position of maximum froth stability is independent of temperature at ordinary temperatures.

Discussion of Results.

A study of Figs. 38-50 and particularly 51 allows one to draw the following conclusions:-

1. As one ascends the homologous series the froth stability of the solutions increases, i.e. the longer the non-polar chain the more stable the froth.
2. For each concentration range there is a well-defined maximum value (becoming sharper on ascending the series) occurring at a comparatively low concentration of alcohol.
3. With increase in molecular weight i.e. increase in size of the non-polar group, the concentration of alcohol required to give the maximum froth stability decreases. The estimated molar concentration for maximum froth stability for the various alcohols tested is given below in Table XIX.
4. For the isomeric butyl alcohols the froth stability decreases in the order n-; iso-; sec.-; tert-; i.e. as the non-polar chain is successively shortened. This is in agreement with 1 above.
5. For the isomeric butyl alcohols the concentration of alcohol to give maximum froth stability to the solution decreases in the order n-; iso-; sec-; tert.
6. The surface tension corresponding to the concentration of

surface-active substance for maximum froth stability (as obtained from International Critical Tables) is approximately constant. The values are included in Table XIX. This is in agreement with Bartsch.

7. Since these results were obtained, Kyaw Htin (45) using No. 4 Frothing Apparatus has carried out exactly similar tests on the lower aliphatic acids. His results are shown in Fig. 53 and are included for comparison in Table XIX. They are in agreement with the first three conclusions for the alcohols given above. He explains the apparent anomalous results of acetic acid by assuming that the molecules of acetic acid had associated to a certain extent giving an increased molecular cross-sectional area. From a comparison of the alcohols and their corresponding acids it is clear that the acids have a greater maximum froth stability than the alcohols (about twice that of the alcohol for the lower members), and in general it requires a higher concentration to reach maximum froth stability for the acids than for the alcohols.

These numbered conclusions can now be discussed in more detail.

Conclusions No. 1 is in agreement with the results of Bartsch i.e. that froth stability increased up the homologous series, but it will be remembered that he held that froth stabilities again became less after passing amyl alcohol, due to the rapidly decreasing solubility. Since it has been shown here than n-heptyl alcohol solutions have a

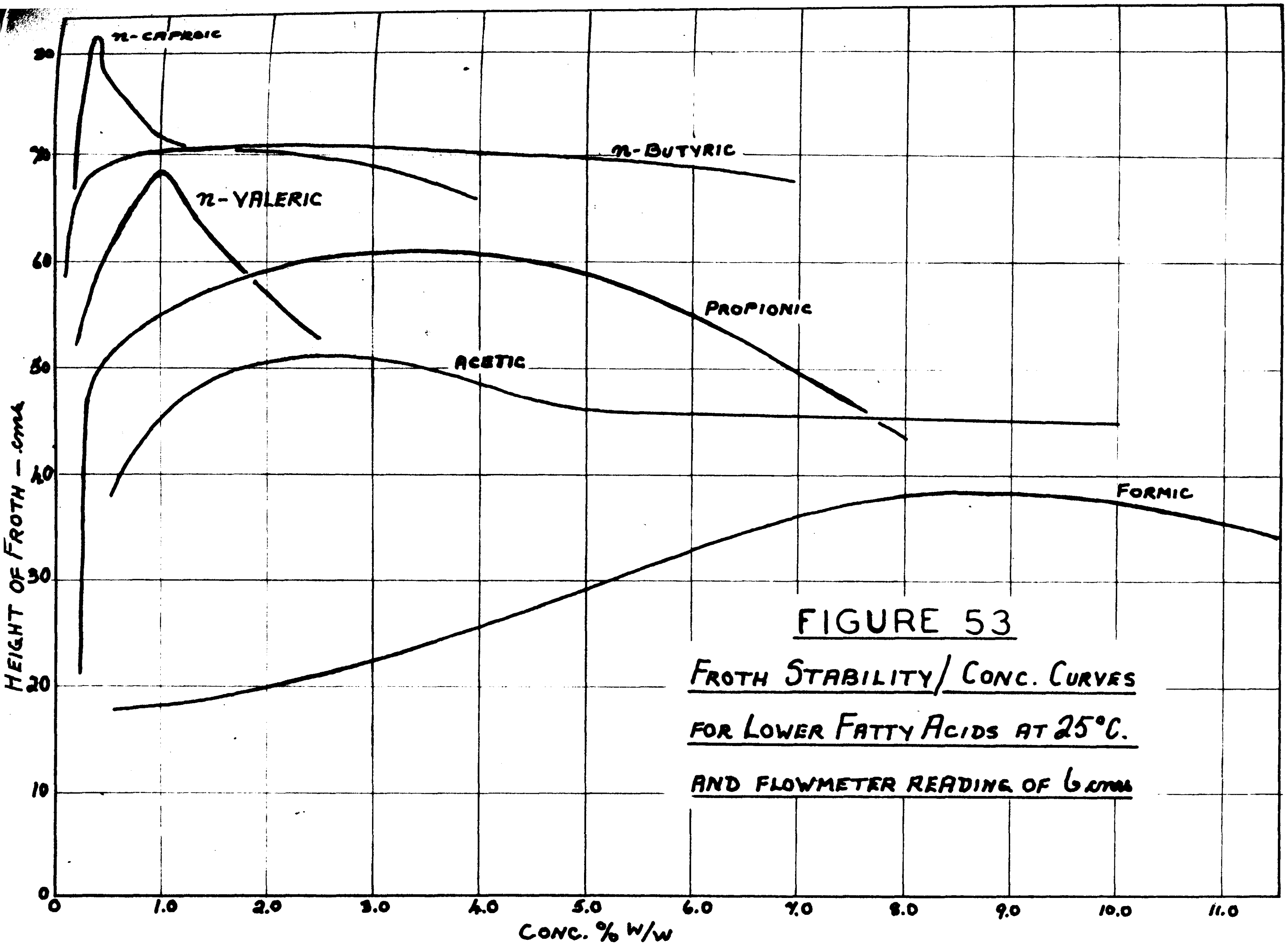


FIGURE 53

FROTH STABILITY/CONC. CURVES FOR LOWER FATTY ACIDS AT 25°C. AND FLOWMETER READING OF 6 cms greater stability than those of n-amyl alcohol it seems that the optimum alcohol lies higher up the series than Bartsch imagined. For the sake of completeness Bartsch's results for alcohols and acids are given in Table XVI, together with results obtained by Sasaki (36) for similar compounds. The latter used dynamic froth height as a measure of froth stability. Thus while Bartsch shows that the highest froth stability for the alcohols tested occurs at Iso-amyl alcohol, and for the acids at Heptylic acid, Sasaki finds the optimum alcohol to be n-Hexanol. Again, using a frothing tube Constable and Erkut (37) found that the maximum height for Octyl alcohol solutions was greater than that for Heptyl alcohol, and Talmud and Suchowolskaja (33) that froths from Caprylic Acid solutions were more stable than those from Heptylic acid solutions. It is therefore felt that in the light of these and our own results that solutions of an aliphatic alcohol showing the greatest froth stability will probably be those of n-Octyl alcohol, while the optimum fatty acid may be Heptylic or Capryluc Acid. Conclusion No. 4 is also relevant here in that it shows that a branched non-polar chain imparts a lower froth stability than does the straight chain of the isomeric alcohol. Thus froth stability seems to depend on the length of the non-polar carbon chain. It is of interest to note that 4-Heptanol gives approximately the same froth heights as n-Amyl alcohol. This indicates that one carbon added to a four carbon alcohol (n-Butanol)

Table XVI.

Maximum Froth Stabilities as Found by -

	Bartsch (14)			Sasaki (36)		
Compound	Maximum Stability in Seconds	Concentration at Max. Froth Stability (mols./litre)	Solution Surface Tension at Max. Stab. (dynes/cm.)	Froth Height at Max. Stab. (cms.)	Conc. at Max. Stab. (mols/ litre.)	Solution Surface Tension at Max. Stab. (dynes/cm.)
Ethanol	5.0	0.28	66	0.95	1.07	56.9
Propanol	11.0	0.32	56	-	-	-
n-Butanol	-	-	-	3.60	0.126	54.0
iso-Butanol	12.0	0.090	56	-	-	-
iso-Amyl alcohol	17.0	0.036	54	-	-	-
n-Amyl alcohol	-	-	-	3.65	0.0131	53.3
tert-Amyl alcohol	10.0	0.034	61	-	-	-
n-Hexanol	-	-	-	4.56	0.0350	48.6
n-Heptanol	8.0	0.0007	68	-	-	-
n-Octanol	5.0	0.0003	64	1.50	0.00105	54.0
n-Decyl alcohol	-	-	-	1.50	7.33×10^{-5}	55.1
Formic acid	4.0	0.45	70	1.70	1.26	64.8
Acetic acid	8.0	0.20	69	1.95	0.819	61.2
Propionic acid	11.0	0.25	61	-	-	-
Butyric acid	18.0	1.00	33	-	-	-
Valeric acid	9.0	0.015	64	-	-	-
Carroic acid	13.0	0.0075	57	-	-	-
Heptylic acid	15.0	0.0015	60	-	-	-
Caprylic acid	12.0	2.5×10^{-4}	66	-	-	-
Nonylic acid	5.0	7.5×10^{-5}	70	-	-	-

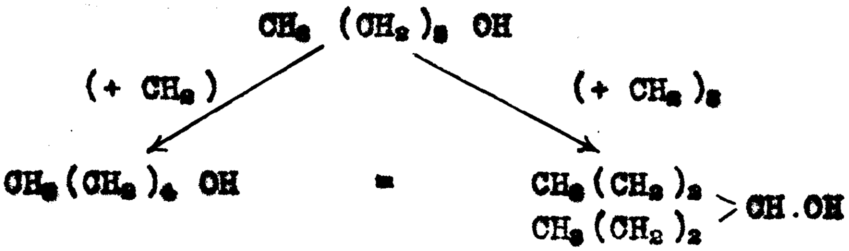
Table XVII.

Froth Stability of 1.50% w/w Isopropanol at 25 ± 0.2°C.

Internal cross sectional area of frothing tube = 1.17 ± 0.01 sq.cm.

Rate of Air Flow		Froth Readings		Length of Froth Column	Volume of Froth	$\log_{10}V$
cu.ft./hr.	ccs./hr.	Bottom	Top			
0.025	708	18.1cms.	18.7cms.	0.6 cms.	0.70ccs.	$\bar{1}.847$
0.050	1417	18.7	19.5	0.8	0.94	$\bar{1}.971$
0.073	2606	19.8	20.4	0.6	0.70	$\bar{1}.847$
0.097	2742	20.0	21.4	1.4	1.64	0.215
0.120	3395	20.6	22.4	1.8	2.11	0.324
0.144	4070	21.3	23.4	2.1	2.46	0.391
0.167	4730	22.1	24.5	2.4	2.81	0.449
0.190	5380	22.9	26.0	3.1	3.63	0.560
0.211	5970	23.9	27.6	3.7	4.33	0.637
0.232	6570	24.9	29.2	4.3	5.04	0.702
0.252	7130	25.5	30.4	4.9	5.74	0.759
0.270	7640	25.7	31.5	5.8	6.79	0.832
0.287	8120	25.4	32.3	6.9	8.08	0.907
0.303	8570	25.2	33.3	8.1	9.48	0.977
0.321	9080	25.0	33.9	8.9	10.41	1.017
0.337	9540	24.8	34.8	10.0	11.80	1.072
0.353	9990	24.5	35.7	11.2	13.20	1.121
0.367	10390	24.0	36.2	12.2	14.40	1.158
0.382	10830	23.6	36.8	13.2	15.58	1.193
0.395	11180	22.9	37.6	14.7	17.35	1.239

in the n-position has as much effect on the froth stability as three added in the secondary position, i.e.



$$\begin{tikzcd} & CH_3(CH_2)_3\ OH \arrow[dl, "(+\ CH_2)"'] \arrow[dr, "(+\ CH_2)_3"] & \\ CH_3(CH_2)_4\ OH & = & \begin{matrix} CH_3(CH_2)_2 \\ CH_3(CH_2)_2 \end{matrix} > CH.OH \end{tikzcd}$$

The Froth Volume Stability Constant was evaluated for the solutions of maximum stability of the alcohols tested in this work. Solutions of a concentration having the maximum froth stability for each alcohol were prepared in double distilled water. Frothing tests were carried out with 20 ccs. of each alcohol solution in the No. 5 apparatus. The length of froth column produced over a range of air-flow was measured, and from the results obtained (plotted in Figure 54) and tabulated as in the specimen Table XVII, the linear plots of rate of air flow against log. volume of froth were derived as in Figure 55. The values of M and N were then calculated as explained in the previous section. The values are given in Table XVIII below.

Table XVIII /

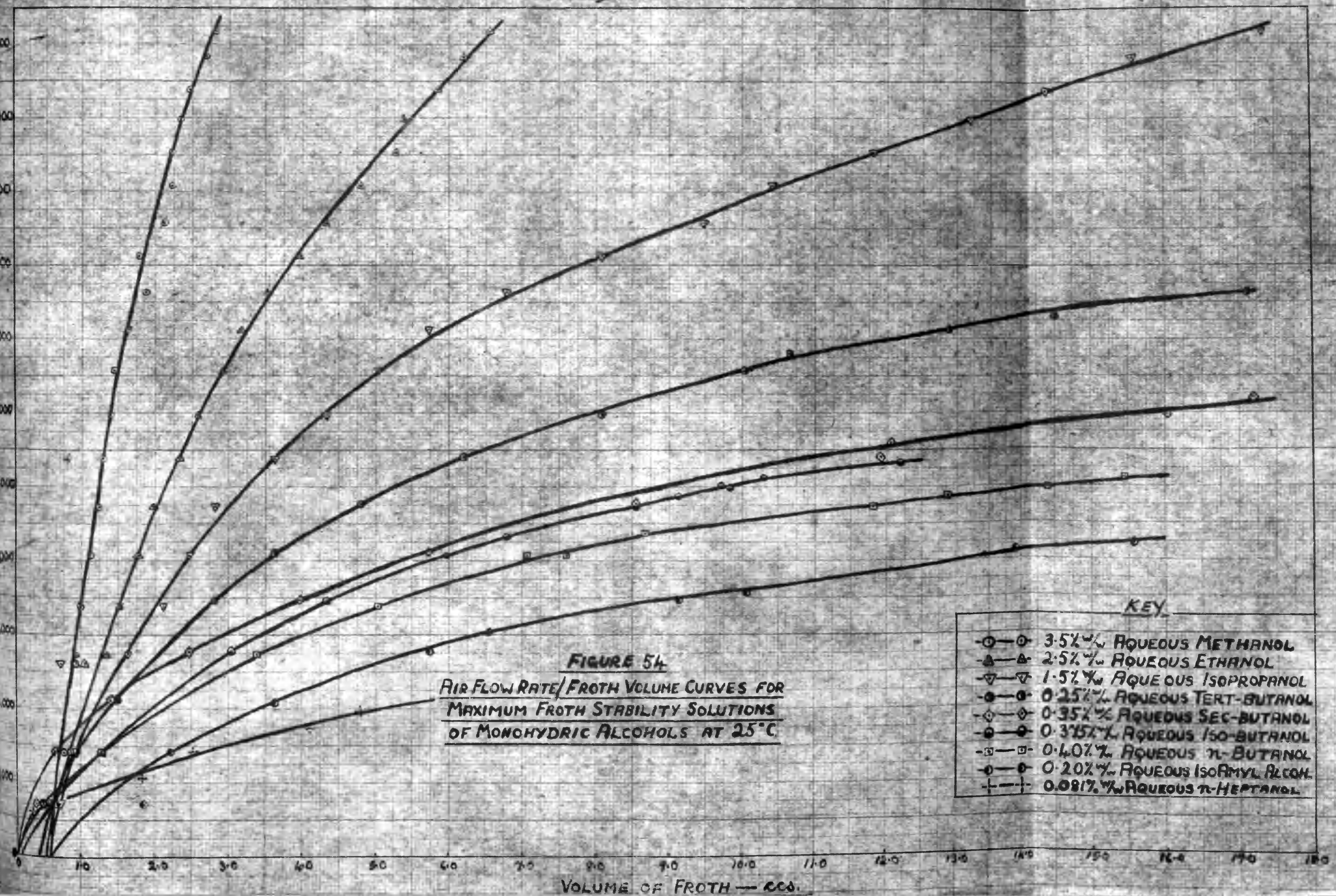


FIGURE 54

AIR FLOW RATE/FROTH VOLUME CURVES FOR MAXIMUM FROTH STABILITY SOLUTIONS OF MONOHYDRIC ALCOHOLS AT 25°C

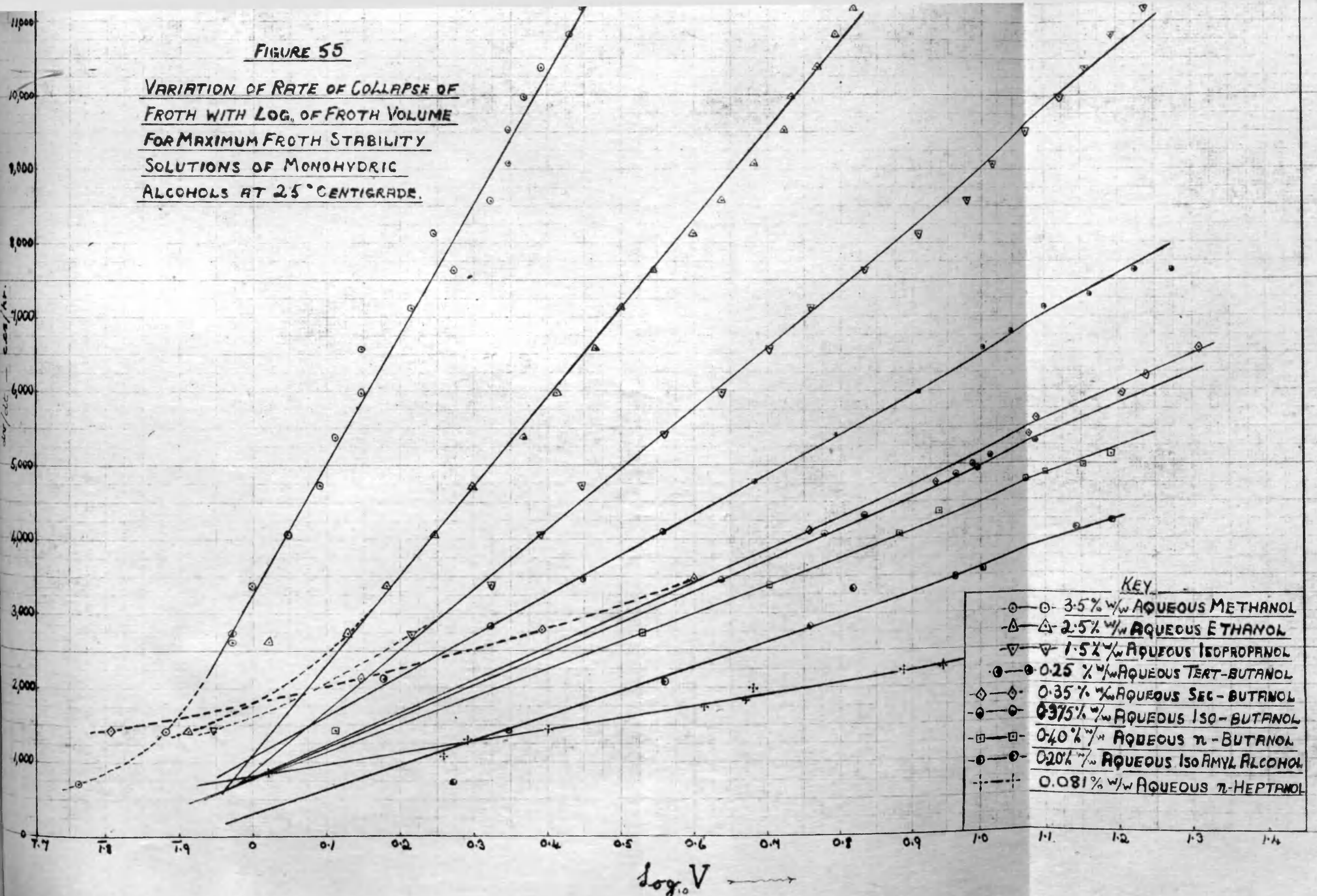


FIGURE 55

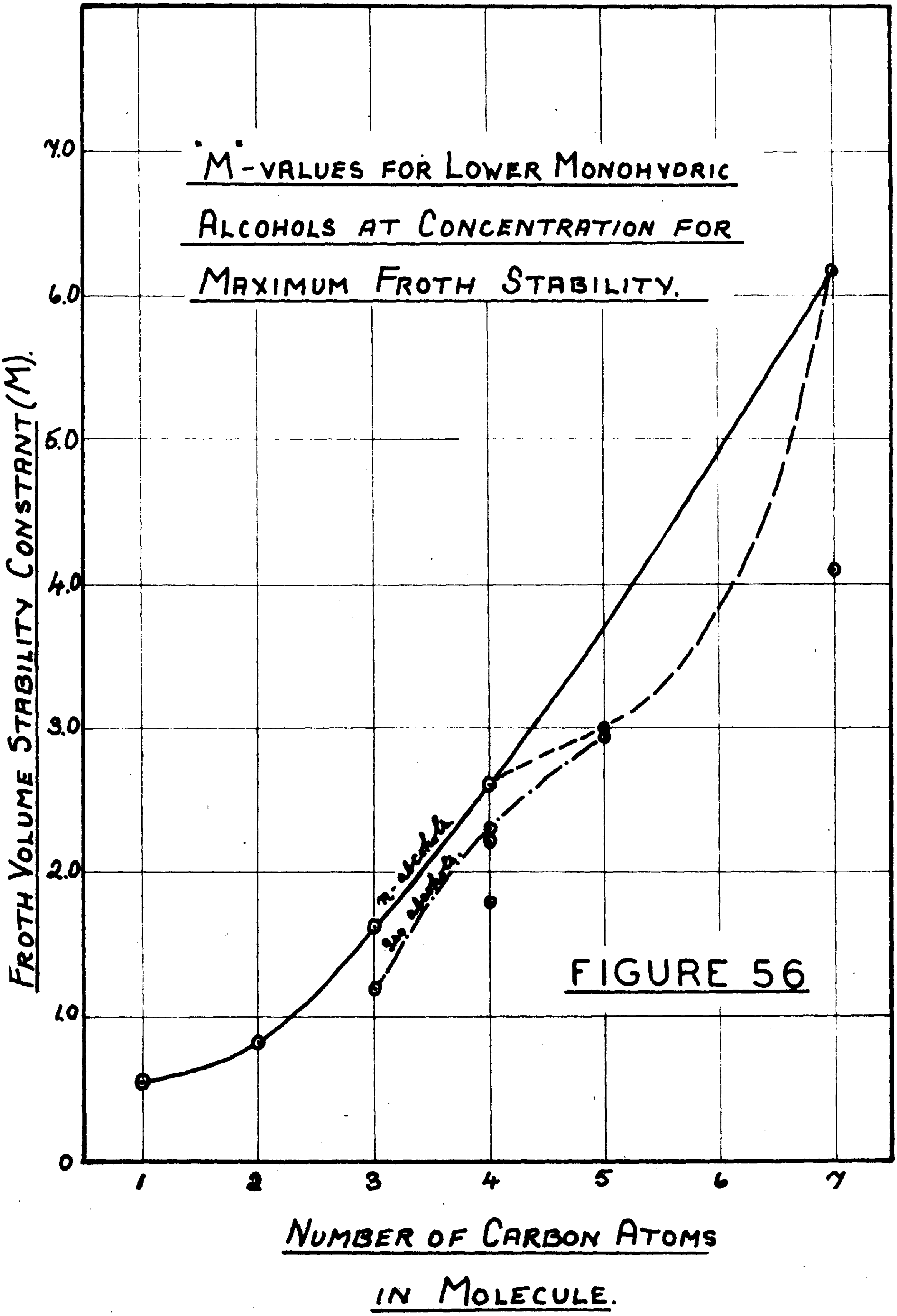
VARIATION OF RATE OF COLLAPSE OF FROTH WITH LOG.₁₀ OF FROTH VOLUME FOR MAXIMUM FROTH STABILITY SOLUTIONS OF MONOHYDRIC ALCOHOLS AT 25° CENTIGRADE.

Table XVIII

Stability Constants for lower Monohydric Alcohols at 25° ± 0.2°C.

Alcohol	Concentration for Max. Froth Stab. (% w/w)	M	N
Methanol	3.50	0.551	0.654
Ethanol	2.50	0.802	0.808
n-Propanol	1.20	1.614	0.945
iso-Propanol	1.50	1.189	0.776
n-Butanol	0.400	2.608	0.617
iso-Butanol	0.375	2.304	0.649
sec-Butanol	0.350	2.215	0.654
tert-Butanol	0.250	1.789	0.632
n-Amyl	0.140	2.984	1.128
iso-Amyl	0.200	2.944	0.805
n-Heptanol	0.081	6.17	0.305
4-Heptanol	50% sat. soln.	4.09	0.532

The appropriate values for Sec. Heptanol were extracted from Table X and again included here. The results for n-Propanol and n-Amyl alcohol are not included in Figures 54 and 55 as they have already been given in the earlier part of this work in the preparation of Table VI and Figure 34. The values of M are plotted in Figure 56 against the number of carbon atoms in the alcohol, and it can be seen that M increases steadily with the length of the non-polar chain in the n-alcohols. The value for n-Amyl alcohol does not fall close to the full-line curve, but it may be that the true shape of the curve is as shown dotted. This could be verified from measurements with n-Hexanol. Unfortunately this material was not available at the time of carrying out



"M"-VALUES FOR LOWER MONOHYDRIC ALCOHOLS AT CONCENTRATION FOR MAXIMUM FROTH STABILITY.

FIGURE 56

these tests. The chain-dotted curve shows the variation of M for the iso- alcohols tested.

The value of N is remarkably constant for all these materials. It is therefore felt that N is really an "apparatus" constant and varies only with the linear dimensions of the apparatus, initial volume of solution, etc. This was also indicated by the results of Table X.

In conjunction with conclusion No. 6 it should be recalled, as mentioned earlier, that the static surface tension value at maximum froth stability is less interesting than the change in free energy of the surface from the dynamic surface tension of the surface at zero time before adsorption starts to the static surface tension when adsorption is complete. As this, in the cases being discussed, constitutes a decrease in surface tension one may speak of a "loosening" of the surface which provides the solution with a latent ability to froth. Since the solutions under consideration are relatively dilute their dynamic surface tension will approach that of pure water and thus from conclusion No. 6 it seems that at maximum froth stability the latent froth forming ability of all the solutions is approximately equal.

Constable and Erkut (37) by combining the equations of Gibbs and Szyszkowski, and again by combining the equations of Schofield and Rideal and of Szyszkowski, have sought with limited success to show that for surface active substances of low solubility the maximum froth stability will occur in the region of 40-50% saturation in water. They give experimenta results showing that for aqueous solutions of Heptanol and of Heptoic and Caprylic acid the maximum stability is near 40% saturation. This is in agreement with the results given here for the Heptanols.

The remaining conclusions given above if grouped together, naturally lead one to consider the concentration of surface-active agent in the surface film of the bubbles. It is easy to fall into the error of drawing conclusions from the various bulk concentrations of surface-active agents in solution necessary for maximum froth stability, but it is the concentration of surface-active agent actually in the surface layer which contributes to the stability of the bubble film. This concentration is not merely proportional to the bulk concentration but is connected to it by the Gibbs' adsorption equation. By utilising this equation the number of frother molecules in unit area of the bubble film can be estimated. Since none of the substances tested forms insoluble films on water at the dilutions involved, the Gibbs' equation may be expected to hold more or less accurately. Thus using the surface tension/concentration curve for each substance the excess of frothing agent in the surface film can be calculated.

The surface tension/concentration curves were plotted from figures given in International Critical Tables (46). In some cases these were not available at 25°C, but, since the

Table XIX.

Frothing of Solutions at 25°C.

Compound	Max. Froth Height in No. 4. Apparatus (cm.)	Concentration for Max. Froth Stability w/w %	Moles. 1 litre	Molar %	Surface Tension at Max. Stab. (dyne/cm.)	$\frac{ds}{dc}$ dynes/cm moles/litre.	UN moles. per sq.cm.	$\frac{1}{UN}$ A per mol.	Refs.
Formic Acid	38.0	8.75	1.90	3.62	64	-2.74	1.27x10	78.8	(47)
Methanol	18.8	3.50	1.09	2.00	64	-5.68	1.50 "	66.7	(47)
Acetic Acid	51.0	2.50	0.417	0.747	65	-12.5	1.27 "	78.8	(47)
Ethanol	25.8	2.50	0.544	0.990	61	-14.3	1.88 "	53.2	(48)
Propionic Acid	61.0	3.50	0.473	0.848	54	-16.1	2.24 "	44.7	(49)
n-Propanol	44.6	1.20	0.202	0.373	61	-44.7	2.20 "	45.6	(51)
iso-Propanol	37.8	1.50	0.250	0.450	60	-33.0	2.01 "	49.8	(51)
n-Butyric acid	70.5	2.50	0.284	0.510	47	-36.3	2.64 "	37.9	(49) & (50)
n-Butanol	57.4	0.400	0.054	0.098	62	-	-	-	-
iso-Butanol	53.2	0.375	0.051	0.092	62	-112	1.38 "	72.4	(51)
sec-Butanol	49.6	0.350	0.047	0.081	-	-	-	-	-
tert-Butanol	43.8	0.250	0.034	0.061	-	-	-	-	-
Valeric Acid	67.5	1.00	0.098	0.176	40	-119	2.84 "	35.2	(49)
n-Amyl alcohol	62.6	0.140	0.016	0.029	59	-507	1.97 "	50.8	(47)
iso-Amyl alcohol	60.0	0.200	0.023	0.041	57	-398	2.20 "	45.4	(47)
Caproic Acid	82.0	0.035	0.0030	0.0054	66	-1680	1.23 "	81.3	(50)

value of $\frac{ds}{dc}$ does not change much with temperature, and since it has been already found that the position of maximum stability is little affected by change in temperature, values at 30°C or 20°C were substituted where these only were available. The value of the tangent, $\frac{ds}{dc}$, to the curve at the required concentration was computed and the required quantity calculated as shown below in the specimen calculation,

Specimen Calculation -

Gibbs' equation is $U = \frac{-c}{RT} \cdot \frac{ds}{dc}$

Where U is the excess concentration of surface active agent per square cm. of surface.

Thus UN is the excess number of molecules per square cm. of surface, where N is Avogadro's Number = 6.023 x 10

$R = 8.316 \times 10^{7}$ ergs per degree

$T = 298°$ absolute

$\therefore \quad UN = - k.c. \frac{ds}{dc}$

where k is a constant $= \frac{N}{RT}$, here $= 2.431 \times 10^{13}$

For ethanol at maximum froth stability $c = 2.50\%$ w/w = 0.544 moles. per litre and from the surface tension/concentr tion curve plotted from the I.C.T. figures, at 0.544 moles. per litre $\frac{ds}{dc} = -14.3$

Thus $UN = -2.431 \times 10^{13} \times 0.544 \times (-14.3)$

1.88×10^{14} molecules per square cm.

The values of UN for the other compounds are given in Table XIX together with the references from which the I.C.T. took the surface tension/concentration values. In some cases no suitable figures were available at all.

Considering the large possible errors in the evaluation of UN, such as errors in the original surface tension determinations; errors in drawing a smooth curve through the points; errors in the graphical determination of the tangent to the curve at the required concentration value; and errors in the original determination of this concentration for maximum froth stability, a study of the values of UN obtained shows that they are remarkably constant. By taking the reciprocal of UN a value is obtained for the effective area of surface per molecule of surface active agent. This constancy of UN means that the surface-active molecules must all have the same cross-sectional area in the adsorbed position, and this can only occur for such unlike molecules as acetic acid (with two carbon atoms) and caproic acid (with six carbon atoms) if they are oriented in the surface as demanded by the Langmuir-Harkins, that is, they are standing in the surface with the non-polar group in the gas phase and the polar group in the aqueous phase. The results of Table XIX are thus an indirect proof that the orientation theory holds for these comparatively small and completely soluble molecules as it does for the larger molecules.

The second point emerging from the results is that maximum froth stability corresponds to a definite concentration in the surface film, independent of the size of the non-polar end of the molecule but in some way related to the cross-sectional area of the surface-active molecule. X-ray measurements on crystals of the fatty acids have shown the cross-sectional area of the molecules to be about 15Å Measurements on the compression of insoluble films of fatty acids, alcohols, etc., on water, give figures of 20.5 Å for the cross-sectional area of the fatty acids (R.COOH) and 21.6 Å for the alcohols (R.CH$_2$OH). These figures show that at maximum froth stability the frother molecules in the surface of the bubble are by no means closely packed, since, from the results of Table XIX it seems that each molecule is permitted about two to three times its necessary free area on the surface.

Talmud and Suchowolskaja (33) measured the life of bubbles at a water surface coated with insoluble films of long chain fatty acids, etc. The concentration of reagent per unit area of surface was varied by lateral compression of the film. They were thus able to determine the surface concentration required for maximum stability of the bubble. The results they obtained for films on pure water are given below in Table XX.

Table XX.

(After Talmud and Suchowolskaja (33))

Substance in Film	Surface Concentration for Maximum Stability Moles.10^{-10} /cm.^{2}	Surface Concentration for Maximum Stability Molecules/cm.^{2}	Area per Molecule Å^2
Palmitic Acid	3.06	1.84×10^{14}	54.4
Stearic Acid	5.08	3.06×10^{14}	32.7
Oleic Acid	2.73	1.64×10^{14}	61.0
Cetyl Alcohol	2.30	1.39×10^{14}	72.3
Ethyl Oleate	0.89	0.536×10^{14}	187

It can be seen at once that their figures for area per molecule at maximum stability are in excellent agreement with those obtained in this work and already given in Table XIX.

Adams (52) rather doubts the results of Table XX in that the area per molecule is greater than that which coherent films can occupy and claims that the variation of surface tension with area per molecule in the films is practically zero at these areas. Since, however, froth stability is essentially bound up with the architecture of the bubble film, it will depend not only on the resistance to rupture of the air/liquid interface but also on the rate of drainage of water molecules from the film. Thus while it has been shown that with a constant polar group the stability increases with the length of the non-polar chain, the concentration of frother molecules in the surface film for maximum stability will depend on the ability of the polar group to prevent drainage of water molecules. It will do this through its power to attract water molecules. If it is assumed that each polar group can attract and hold a definite number of water molecules, a state will be reached as the concentration of frother molecules is increased where the maximum number of water molecules per unit area of film are held by the force of attraction. This will be the point of maximum stability of the film. At a higher surface concentration than this the frother molecules will be packed sufficiently close for their polar groups to be within the field of attraction of each other, the overall effect of which will reduce the effective attractive force for water molecules. Drainage will then be quicker and the films less stable. The most stable film therefore will not be a coherent film of frother molecules but one having a configuration made up of frother and water molecules in a definite ratio, and the bulk concentration of soluble surface-active substance for maximum froth stability is that giving this ratio in the surface film.

PINE OIL AS A FLOTATION REAGENT.

Although the lower monohydric alcohols are ideal surface-active agents for a theoretical study, the majority are too soluble in water, i.e. their non-polar chain is too short, to make them practical frothers. Amyl alcohol is perhaps the smallest molecular weight alcohol used in practice. Even here the compound is used as in Fusel Oil, where it is no doubt mixed with alcohols of greater molecular weight. Since, as indicated earlier, the majority of industrial frothers are impure compounds or deliberate mixtures, the difficulties of a study into their mode are thereby increased. Unless one studies singly the components of the mixture and their various influences on the mode of action of the reagent, one can never be sure that results given by one particular sample of an industrial frother will be duplicated by another. It was decided, therefore, to apply this method of attack to Pine Oil, perhaps one of the most widely used frothers in mineral froth flotation.

Pine oil has long been used as a "frother" for the flotation of minerals, yet there is very little to be found in the literature about its chemical and physical properties in relation to froth flotation. This is rather surprising in view of its extensive use, but is no doubt due to the fact tha it is a natural product, a complex mixture of terpene derivatives, and thus subject to a certain amount of variation.

The production from the processed wood of American pine trees, chiefly the American long-leaf pine (Pinus palustris), but also from other southern pines as the slash pine (Pinus heterophylla), the short-leaf pine (Pinus echinata), the Loblolly pine (Pinus taeda), the spruce pine (Pinus glabra) the yellow pine (Pinus ponderosa), etc. has been well described in a number of papers. (53), (54), (55), (56), (57). Pine Oil really occurs as a byproduct in the production of "wood" turpentine from waste pine wood. The wasteful American methods of harvesting turpentine in which the trees tend to be "tapped to death" has left large quantities of waste wood in the pine forests in the form of dead and fallen timber, together with hugh numbers of pine tree stumps. These still contain proportions of oleo-resins and have become valuable raw material in the production of "wood" turpentine and Pine Oil. In outline, the process consists in the shredding of the wood to small chips, the extraction of the wood with steam to remove the turpentine and part of the Pine Oil, followed by extraction with petroleum naphtha to remove the remaining Pine Oil and rosin. The turpentine and Pine Oil are subsequently separated by fractional distillation In a modern version of the process the use of steam is omitted and turpentine, Pine Oil, and rosin are extracted from the wood by a volatile solvent, and separated by fractional distillation leaving crude wood rosin as residue in the still. Humphrey (55) gives a figure of 12 gallons of volatile terpene oils per ton of wood.

Composition of Pine Oil.

In spite of its complexity the composition of Pine Oil seems to be fairly well established. Teeple (53) showed that it contained α-terpineol by the production of terpin hydrate on shaking the oil with sulphuric acid. Schimmel and Co. (59) examined systematically the oil from the stumps of Pinus palustris and found that it contained:-

(a) the hydrocarbons,

α-Pinene, β-Pinene, Camphene, l-Limonene, Dipentent, Terpinene, Terpinolene.

(b) the alcohols,

α-Terpineol, Borneol, Fenchyl alcohol, and probably iso-Fenchyl alcohol.

(c) the phenol ether, methyl chavicol.

(d) the oxide, Cineol.

(e) the ketone, camphor.

Adams (60) investigated the oils from different species, but unfortunately after fractionating the oil he only examined the fraction boiling below 160°C. In the wood oil of the single-leaf nut pine (Pinus monophylla) he identified d-α- Pinene and possibly β-Pinene, and of Pinus ponderosa he identified α- and β-Pinenes and Limonene. Benson and Darrin (61) identified Terpineol in Pine Oil from the Douglas Fir. In 1923 Gill reported that he had identified iso-Fenchyl alcohol and l-menthone in a sample of oil (62)

More recently, dihydro terpineol and small amounts of verbenone have been found in U.S. Pine Oil (63) and Humphrey (56) states that the borneol separated from Pine Oil contains approximately 10% of Isoborneol.

As is to be expected it appears that there is a wide possible variation in the proportion of the various constituents present. The terpene alcohols constitute the greater proportion of the oil, the best quality oil containing not more than 5% of hydrocarbons. The following approximate analysis of Pine Oil is given by Pickett and Schantz (64).

Constituent	Per cent.
α-Terpineol	50 - 60
Other Terpineols	15 - 25
Borneol	5 - 10
Fenchyl Alcohol	5 - 10
Terpene Ethers	5 - 10
Ketones and Phenols	1 - 2

More recently, Bishop (53) gives the approximate composition of Yarmor F. flotation grade Pine Oil, as,

Tertiary Alcohols (chiefly Terpineol)	55 - 65
Secondary alcohols (Borneol, Fenchyl Alcohol)	10 - 20
Hydrocarbons (monocyclic terpenes such as dipentene)	10 - 20
Ethers (anethole, methyl chavicol)	5 - 10
Ketones (camphor)	5 - 10

Physical Constants.

The most interesting of the physical constants of Pine Oil are the Distillation Range, the Specific Gravity, and the Refractive Index. A reference table of these constants for the various key components of Pine Oil is given below. The compounds are arranged in order of increasing Boiling Point down the table.

Table XXI.

Constants of the Principal Components of Pine Oil.

Substance	Boiling Point	Specific Gravity	Refractive Index
α-Pinene	154°C	$0.8582\,^{20^\circ}_{4^\circ}$	$1.4658\,^{20^\circ}_{D}$
Camphene	159 "	0.879 "	-
Dipentene	176 "	0.8425 "	1.4730 "
Terpinene	180 "	0.846 "	1.4846 "
Terpinolene	185 "	0.855 "	1.4823 "
Fenchyl Alcohol	201 "	0.942 "	1.4703 "
Camphor	209 "	$0.990\,^{26^\circ}_{4^\circ}$	-
Dihydroterpineol	210 "	$0.901\,^{20^\circ}_{20^\circ}$	1.4630 "
Borneol	212 "	$1.011\,^{20^\circ}_{4^\circ}$	-
Methyl Chavicol	215 "	$0.9645\,^{21^\circ}_{4^\circ}$	$1.5244\,^{16^\circ}_{D}$
α-Terpineol	219.8 "	$0.9357\,^{20^\circ}_{4^\circ}$	$1.4831\,^{20^\circ}_{D}$
Anethole	233 "	$0.9936\,^{15^\circ}_{15^\circ}$	1.5613 "

The Specific Rotation of the various components might also be listed, but so many of them are optically active that there is much mutual cancellation of rotation in the oil to give it a low value either dextra- or laevo-.

It can be seen from the above table that if Pine Oil is to contain a minimum of hydrocarbons, as stated by Humphrey, there must be little distillation below 200°C. For instance the sample examined by Teeple (58) started distillation at 206-210°C, 75% distilled between 211° and 218°C, and 50% between 215° and 217°C. The sample of Schimmel & Co. (59) started distilling at 156°C, 5% distilled between 160° and 190°C and the bulk between 190° and 220°C; thus it is to be expected that they would find a fair proportion of hydrocarbons, as was the case. As an example of an oil coming between these extremes we have that of the Douglas Fir examined by Benson and Darrin (61) which distilled between 175° and 260°C, 57% distilling between 214° and 226°C, and 33% between 218° and 222°C. Bishop (53) gives the typical distillation range for Yarmor F. shown below in table XXII. It is instructive to compare the figures with the Boiling Points of table XXI.

Table XXII.

Distillation Range for Yarmor F. Pine Oil (A.S.T.M.)

Per Cent	Degree Centigrade	Per Cent	Degree Centigrade
5	201.7	70	215.6
10	204.0	90	219.3
30	209.0	95	222.6
50	212.9		

A study of the Specific Gravities of Table XXI shows that the "active" components of the Pine Oil, i.e. the alcohols, have higher values than the hydrocarbons. Thus one would expect the best quality Pine Oil to have a Specific Gravity near the upper end of the range, e.g. about 0.93, near the Specific Gravity of its chief component, Terpineol.

Again, since the Refractive Indices of the components are fairly near each other, one would expect the Refractive Index of Pine Oil to be near that of Terpineol, i.e. about 1.48. e.g. the sample of,

Teeple n_D^{20} = 1.4830
Schimmel & Co. n_D^{20} = 1.4853
Benson & Darrin, n_D^{20} = 1.4818
Bishop, n_D^{20} = 1.4803

Thus the constants for the best grade of Pine Oil, i.e. with maximum alcohol content, should approximately be,

Distillation Range = 200 - 225°C.
Specific Gravity = 0.93
Refractive Index (n_D^{20}) = 1.48

The Flotation Properties of Pine Oil.

The reason for the continued use of Pine Oil as a frother in the presence of so many synthetic agents which can be "tailor-made" to produce desired results lies in the fact that it possesses all the attributes of the ideal frother discussed at the beginning of this work. Apart from possessing the "duplex" character defined there the terpene hydrocarbons of Pine Oil have the added advantage that the unsaturated linkages make them slightly surface-active and more easily emulsified with water. This tends to prevent the froth from becoming too oily, and permits easy extraction of terpene alcohol into the aqueous phase. The alcohol remaining in the undissolved hydrocarbon phase renders it highly surface-active so that extremely small quantities of reagent are effective (0.05 - 0.10 lbs. per ton of ore). Thus, although the froth is less brittle than that produced by pure Cresol or by the higher alcohols, it is not so tough nor has the oily characteristics of that produced by Creosote oils like Barrett No. 4.

Terpineol, the chief component of Pine Oil, has been much used in flotation experiments as a standard frother, (65) but very little work has been done on the other components.

Taggart, Taylor and Ince (66) in their large classification of flotation agents, class Terpineol as "excellent", and Borneol and Camphor as "good" frothers. Bishop (53) indicates that the terpene ethers also have considerable merit as frothers. This last author showed how the polar group of Terpineol includes not only the Hydroxyl group but also the double bond by comparing in similar flotation tests, Terpineol, Dihydro-terpineol, and Pine Oil. His results are given in Table XXIII below.

Table /

Table XXIII

Flotation Tests on a Lead Ore (Galena in a Dolomite gangue) (after Bishop).

Frother		Assay for Lead (%)			
Description	lb./ton	In Tailing	In Concentrate	Recovery (%)	Quality of Froth
α-terpineol	0.12	0.56	59.9	87	Good
Dihydro-α-terpineol	0.12	1.03	64.2	76	Fair
Pine Oil	0.12	0.57	65.7	87	Good
Other reagents: (in each test)					
Potassium isopropyl xanthate	0.10				
Sodium Sulphide	0.15				

Bishop also carried out tests with a number of synthetic Pine Oils (mixtures of Terpineol and Dipentene),and, although his results were not very conclusive, they seem to indicate that the blend of terpene derivatives in a flotation grade Pine Oil could not be bettered by a different ratio of the various components nor even by pure terpineol itself.

De Witt (67) made a study of the effect of Pine Oil and its components on the Surface Tension of water. As was to be expected, the hydrocarbons, Pinene, Dipentene, and Terpinolene had little effect on the Surface Tension. For the alcohols, Terpineol, Fenchyl Alcohol and Borneol, the lowering of Surface Tension of a dilute aqueous solution was practically the same. The Surface Tension lowering effect of Camphor per mole. was just a little over half that of Borneol due to the greater solubility of Camphor. Comparison of the Surface Tension lowering effects of Pine Oil and Terpineol shewed that weight for weight Terpineol was more effective. This was presumably due to the fact that in Pine Oil some of the Terpineol must remain locked in the hydrocarbon phase to help it to spread on the bubble film. Thus the Surface Tension effect measured by the authors was only that produced by the Terpineol extracted into the aqueous phase.

Preliminary Work with Pine Oils.

The first samples of Pine Oil made available were very kindly supplied by Messrs Macneill & Slean Ltd. These were designated - "Steam distilled Pine Oil (High Grade)", and "Pine distillate (second quality)", and will be known for the purpose of this work as Pine Oil A and Pine Oil B, respectively.

It was not known at this stage whether these materials would be of flotation grade; and a standard flotation test was required for such materials. A series of preliminary flotation tests was therefore carried out to test and compare Pine Oils A and B, and to develop a method of testing rather than to obtain a final series of figures for these oils.

In deciding the most suitable ore mixture to use in these flotation tests the following factors were taken into consideration:- Supply of ore; ease of separation; time to be consumed in assay of feed and concentrate; practical interest of separation. The separation finally chosen was that of coal from limestone, both of which were easily available and are easily separable by froth flotation. The concentrates and feed can be easily and quickly assayed by determination of ash content; and the production of clean coal is of great interest today.

Flotation Machine.

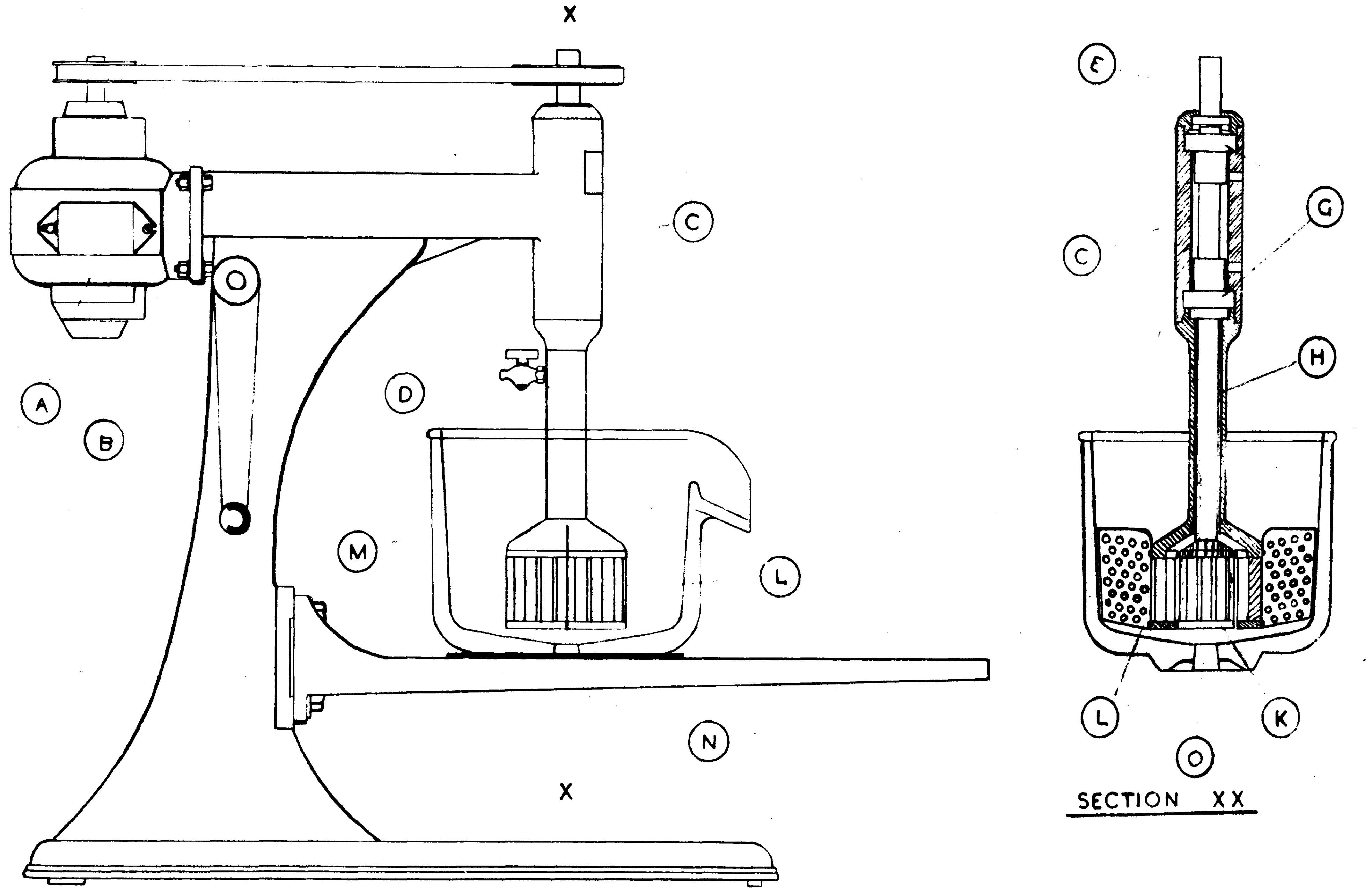
The machine used in these and subsequent flotation tests was a Fagergren laboratory flotation machine manufactured by the American Cyanamid Co. This is a high speed agitation unit with a Pyrex glass cell. It is shown in Figure 57. The rotor-stator assembly of stainless steel and designed for easy cleaning can be raised from or lowered into the glass cell by a hand lever. In operation, the action of the rotor draws air in through the stop-cock provided and down the hollow standpipe into the cell. When this cock is closed air is shut off and the machine becomes an ore conditioning unit, and no frothing of the pulp takes place. An opening normally closed by a rubber bung is provided in the base of the cell for removal of tailing, and the cell itself is easily removable for washing. The recommended solid capacity of the cell is 600 gms. The rotor is belt driven by an 1/8 H.P. electric motor, the speed being controlled by a suitable rheostat. With the setting of the rheostat used the average rotor speeds were measured on a revolution counter.

Average Rotor speed with cell empty = 2300 r.p.m.

Average Rotor speed with cell filled (with pulp specified below). = 1800 r.p.m.

Method of Test.

The feed material was a synthetic mixture of finely ground coal and limestone. The two materials were finely ground separately and not mixed till required for a test. The coal itself had an average ash content of 5.5% and a size distribution as shown in Table XXIV. The limestone was ground to the size distribution shown in Table XXV.



KEY

A- MOTOR
B- HANDLE FOR RAISING ROTOR ASSEMBLY
C- BEARING HOUSING
D- AIR CONTROL PETCOCK
E- ROTOR SHAFT. G- ROTOR BEARINGS
H- STANDPIPE
K- ROTOR L- STATOR
M- CELL N- CELL TABLE
O- TAILING OUTLET (CLOSED BY RUBBER STOPPER)

FIGURE 57

FAGERGREN
LABORATORY FLOTATION
MACHINE

SCALE - 1/4 SIZE

Wm. Gibb

Table XXIV.

Size Distribution of Coal.

Size Mesh	% on Mesh	% Undersize
70	23.2	76.8
80	6.7	70.1
90	10.1	60.0
< 90	60.0	-

Table XXV.

Size Distribution of Limestone.

Size Mesh	% On Mesh	% Undersize
20	10.3	89.7
30	22.6	67.1
40	13.5	53.6
50	10.4	43.2
70	13.2	30.0
80	2.1	27.9
90	4.7	23.2
< 90	23.2	-

A small quantity of Potassium Ethyl Xanthate was used as a supplementary collecting agent in the tests. This was chosen as it has itself no frothing properties.

For each test the following quantities were placed in the cell:-

150 gms. ground limestone

450 gms. ground coal.

2300 c.cs. water containing 25 mgm. of K. Ethyl

Xanthate per litre. The volume was just sufficient to fill the cell without losses through splashing when the rotor was running. The rotor was started and run without the addition of air until all the solid was in suspension. Then a known weight of the Pine Oil was added dropwise and the conditioning of the pulp continued for exactly one minute. When the air cock was opened the froth formed was collected in a suitable vessel till no more came over.

The floated material was filtered, the volume of liquid which had come over as froth measured, the floated solids dried and weighed, and the ash content of the floated concentrate determined by the usual method.

The flotation cell was thoroughly cleaned between tests.

Results.

The results of these tests with Pine Oils A and B are given in Tables XXVI and XXVII, respectively, and plotted in Figures 58 and 59.

The estimation of the recovery of coal by flotation is made difficult by the change in weight that takes place in the limestone ($CaCO_3$) on ashing (to CaO). Representative samples of the feed mixture were taken and the ash content determined.

Average Ash in Feed = 20.7%

This figure, which, due to the change in weight of the limestone, makes it appear that there is more coal in the

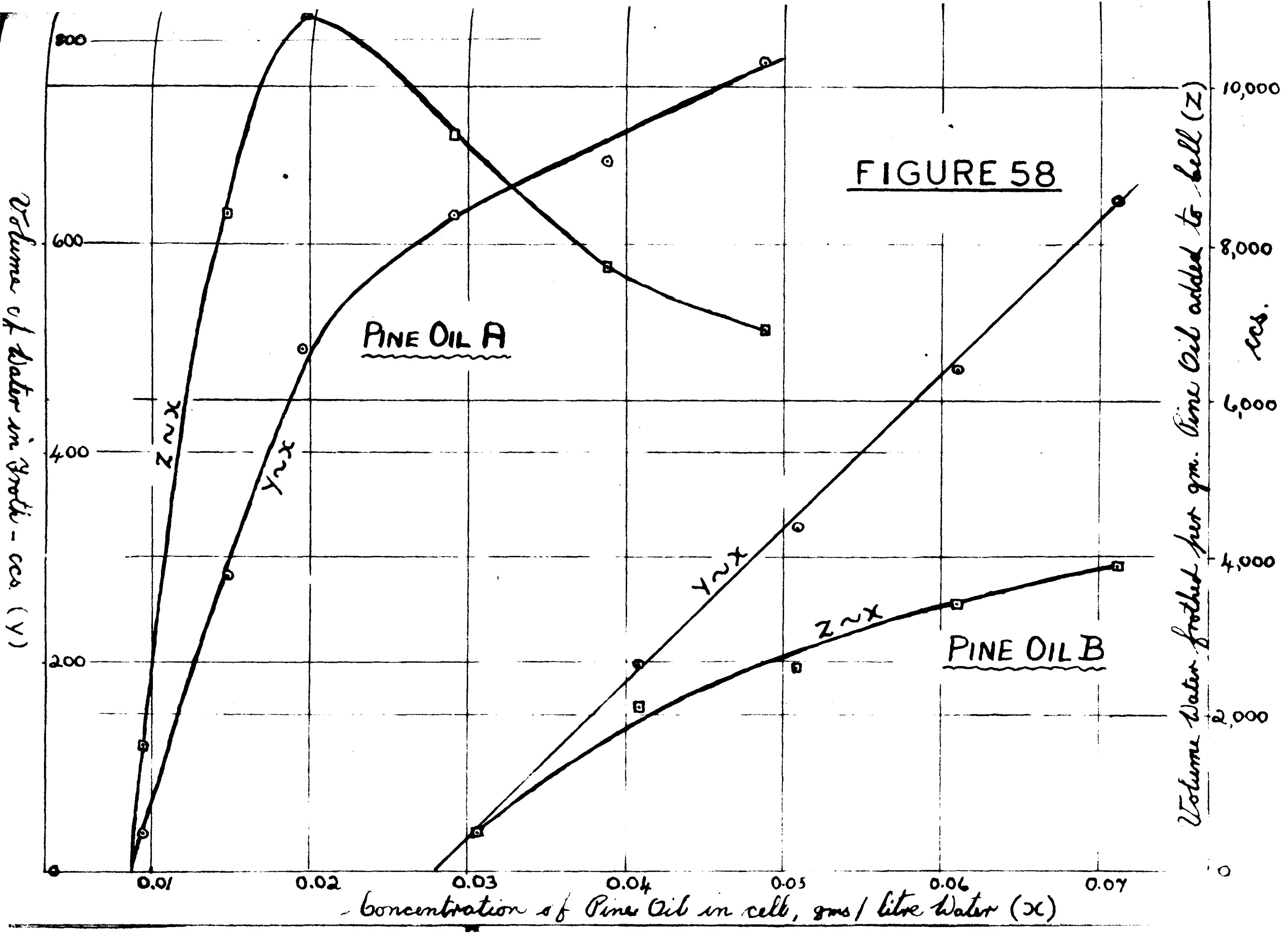


FIGURE 58

PINE OIL A
PINE OIL B
Z~X
Y~X
Y~X
Z~X
Volume of Water in Froth - ccs. (Y)
800
600
400
200
Volume Water frothed per gm. Pine Oil added to Cell (Z)
ccs.
10,000
8,000
6,000
4,000
2,000
0
Concentration of Pine Oil in cell, gms / litre Water (x)
0.01
0.02
0.03
0.04
0.05
0.06
0.07

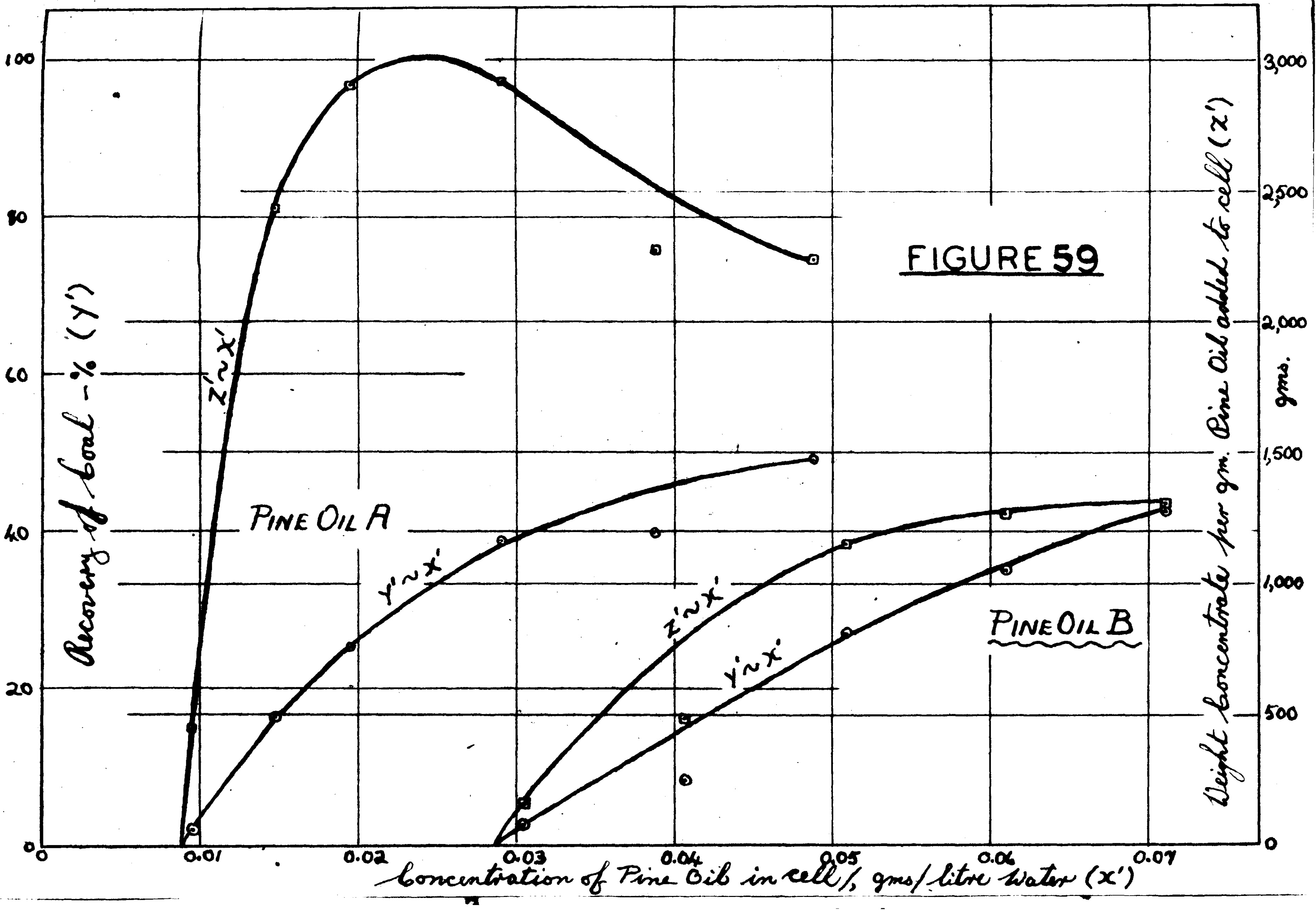


FIGURE 59

Recovery of Coal - % (Y')
Weight Concentrate per gm. Pine Oil added to cell (Z')
gms.
Concentration of Pine Oil in cell, gms/litre water (X')
Pine Oil A
Pine Oil B
Z'~X'
Y'~X'
Z'~X'
Y'~X'
0
20
40
60
80
100
0
500
1,000
1,500
2,000
2,500
3,000
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07

feed than is actually the case, was taken as a basis on which to calculate the recovery. This was used in place of the figure given by the simple addition of the weight of limestone, added to the known weight of ash in the coal. The latter figure would be difficult to apply since it cannot easily be said how much of the ash in the final concentrate was the original ash of the coal and how much the limestone.

Figure 58, gives the curves for the volume of water carried over as froth by the action of the Pine Oils and thus affords a convenient measure of their frothing power. Figure 59 gives the curves for the solid floated in the froth. All the curves are plotted to a base of initial concentration of Pine Oil in cell.

The greater froth stability of Pine Oil A is at once obvious. The actual efficiency of the reagent is better given by the curve connecting volume frothed per gm. Pine Oil added to the cell with concentration of Pine Oil in cell. For Pine Oil A this curve passes through a maximum as the gradient of the "actual volume frothed" curve changes sharply, shewing that the reagent functions best at low concentrations.
At these low concentrations the variation of the volume of water frothed with concentration of Pine Oil is to all intents and purposes linear. This is seen best in the "actual volume frothed" curve for Pine Oil B which is linear for the range tested. This may be caused by the probable low terpene

Table XXVI

Preliminary Flotation Tests - Series I.   Pine Oil A.

Weight Feed = 600 gms.   Per cent ash in feed = 20.7%

Volume of water in cell = 2300 c.cs.

Per cent solids in cell = 20.7%

Collector:- 0.214 lbs. K. Ethyl Xanthate per ton feed.

Test No.	1.	2.	3.	4.	5.	6.
Wt. Pine Oil (gms.)	0.0225	0.0338	0.0450	0.0670	0.0890	0.1125
-do- lbs/ton feed	0.084	0.126	0.168	0.250	0.332	0.420
-do- gms/litre water	0.0094	0.0147	0.0196	0.0291	0.0387	0.0489
Vol. of water frothed (c.cs.)	36.0	282	300	628	680	775
Wt. dried concentrate (gms.)	10.1	82.6	130.9	195.3	202.5	252.5
% Ash in Concentrate	3.4	4.5	5.5	5.2	6.2	7.1
Vol. water frothed/ gm. Oil.	1,600 c.cs.	8,340	11,110	9,380	7,640	6,890
Wt. Concentrate/gm. Oil	448 gms.	2,440	2,910	2,920	2,280	2,240
Concentrate, % Solids	21.9	22.6	20.8	23.7	23.0	24.6
Recovery of Coal,%	2.05	16.6	26.0	38.9	39.9	49.2

Table XXVII.

Preliminary Flotation Tests - Series II. Pine Oil B.

Weight Feed = 600 gms. Per cent Ash in Feed = 20.7%

Volume of water in cell = 2300 c.cs.

Per cent solids in cell = 20.7%

Collector:- 0.214 lbs. K. Ethyl Xanthate per ton feed.

Test No.	1.	2.	3.	4.	5.
Wt. Pine Oil (gms.)	0.0702	0.0936	0.1170	0.1404	0.1638
-do- lbs./ton feed	0.262	0.349	0.436	0.524	0.610
-do- gms/litre water	0.0305	0.0407	0.0509	0.0610	0.0712
Vol. water frothed (c.cs.)	37.5	198	328	480	641
Wt. dried Concentrate (gms.)	12.0	45.6	135.1	178.0	214.0
% Ash in Concentrate	4.5	4.4	5.5	5.8	5.3
Vol. water frothed/ gm. Oil.	534 c.cs.	2,120	2,800	3,420	3,920
Wt. Concentrate/gm Oil	171 gms.	487	1,155	1,267	1,305
Concentrate, % Solids	24.2	18.7	29.2	27.0	25.1
Recovery of Coal (%)	2.40	9.15	26.8	35.2	42.5

alcohol content of B. Thus a much larger range of concentration of Pine Oil B is needed to cover the same range of concentration of terpene alcohol in the cell than is the case for A. Then in terms of terpene alcohol concentration the curve for Pine Oil B becomes merely a magnified portion of that for Pine Oil A.

The "solid" curves of Figure 59 follow more or less the shape of the "liquid frothed" curves. This indicates the importance of froth stability where two reagents under comparison have almost equal collecting power, as in the case here, as shown by the similar ash content of the two sets of concentrate. It can be seen from the Tables that Pine Oil B tends to produce a greater concentration of solid in the froth than does A. This may be due to the fact that although there is probably about the same initial load of ore per bubble in all cases, the lower stability of the Pine Oil B froth causes this initial load to be divided among a smaller number of bubbles in the final overflow. If we take Pine Oil A as being of flotation grade, Pine Oil B is of a much lower standard. To obtain the same recovery of coal one has to use an amount of B that is from two to three times the weight of Pine Oil A required.

Pine Oil G.N.S. No. 5.

A quantity of the flotation grade Pine Oil, G.N.S. No. 5 was kindly supplied by Cyanamid Products Ltd. It was thus decided to compare the physical constants of this oil with the above Pine Oils.

Physical Constants of Pine Oils under test.

A standard distillation test was carried out on the three Pine Oils in turn. The distillation curves obtained are compared in Figure 60. A distillation test was also carried out on the Cyanamid Co. synthetic frothing agent, Frother 60, (this is a synthetic mixture of alcohols and fuel oil), and the distillation curve is included in the diagram.

It can be seen that the curves of Pine Oil, G.N.S. No. 5 and Pine Oil A are very similar, while that of Pine Oil B suggests that it contains about 30% of the constituents of A, plus an unknown higher boiling constituent. From the poor frothing properties of Pine Oil B already noted, it is suggested that this constituent is some high boiling hydrocarbon.

The Specific Gravity, Refractive Index, and Specific Rotation of the three Pine Oils were measured by normal methods. The results are given:-

Specific Gravity

G.N.S. No. 5 $D^{20^\circ}_{4^\circ}$ = 0.9313
Pine Oil A. $D^{20^\circ}_{4^\circ}$ = 0.9272
Pine Oil B. $D^{20^\circ}_{4^\circ}$ = 0.9274
cf. Terpineol $D^{20^\circ}_{4^\circ}$ = 0.9357

Thus G.N.S. No. 5 gives the result nearest to that of Terpineol.

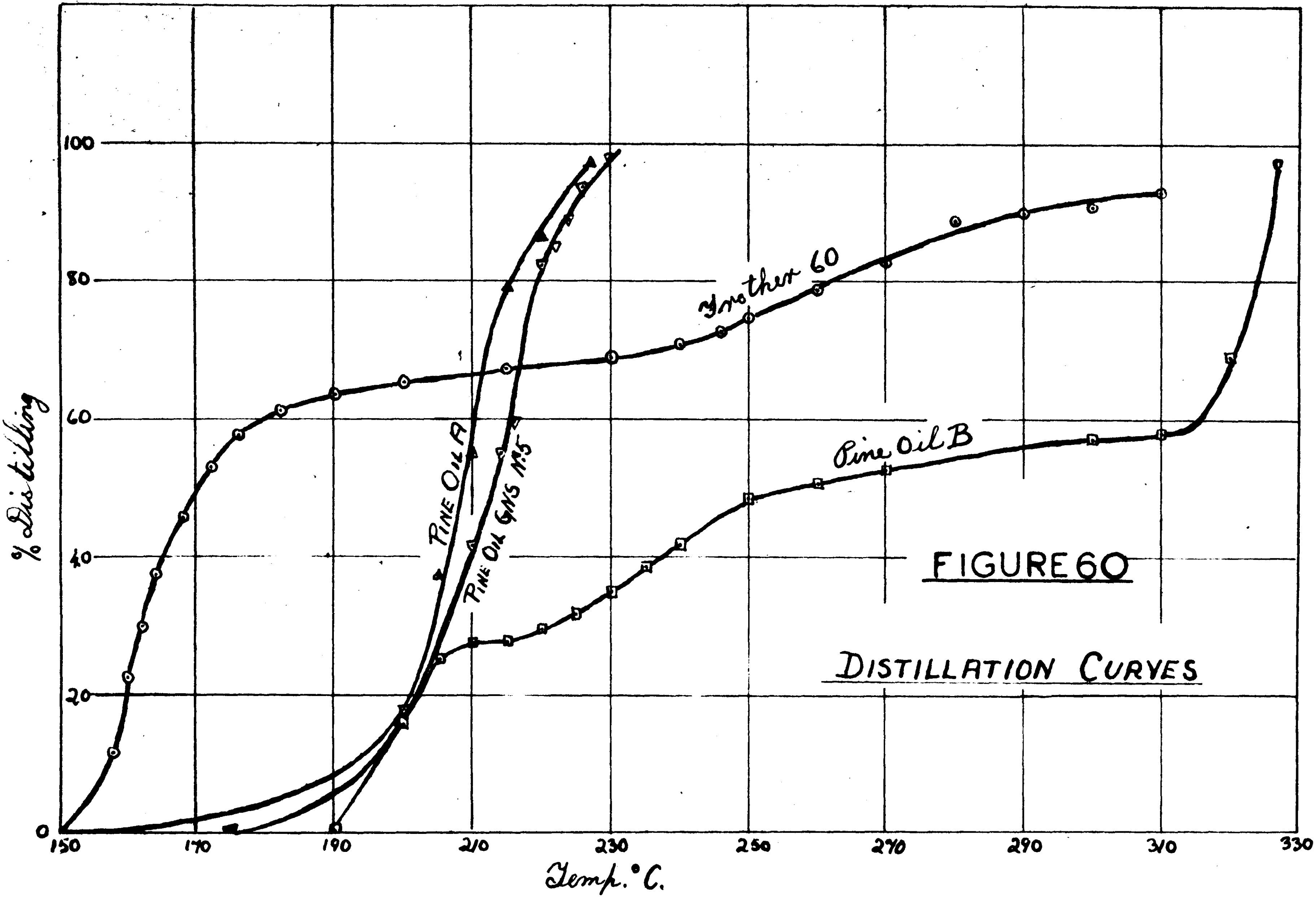


FIGURE 60

DISTILLATION CURVES

Refractive Index

G.N.S. No. 5. n_D^{20} = 1.4827
Pine Oil A. n_D^{20} = 1.4830
Pine Oil B. n_D^{20} = 1.5100
cf. Terpineol n_D^{20} = 1.4831

This time Pine Oil A gives the value nearest to Terpineol and the high refractive index of Pine Oil B shews up its essentially different character.

Specific Rotation.

G.N.S. No. 5. $[\alpha]_D^{20}$ = + 14.11°
Pine Oil A. $[\alpha]_D^{20}$ = + 8.98°
Pine Oil B. $[\alpha]_D^{20}$ = + 0.65°

We would expect from these constants that the frothing properties of G.N.S. No. 5 and Pine Oil A would be very similar, and that Pine Oil B would give different and probably somewhat poorer results.

Absorption Spectra.

As a further means of classification, the Ultra Violet Absorption Spectra of these Pine Oils were determined and plotted in Figure 61. The spectra were determined on a Hilger medium Quartz Spectrograph, E.498. Absorption curves A and C, for Pine Oils A and G.N.S. No. 5 respectively, were obtained from solutions in Ethanol (0.840 gms./litre) and using a 0.5 cm. cell. Curve B, for Pine Oil B, was obtained from a 0.210 gms./litre solution in Ethanol, again using a 0.5 cm. cell. In calculating the molecular extinction for

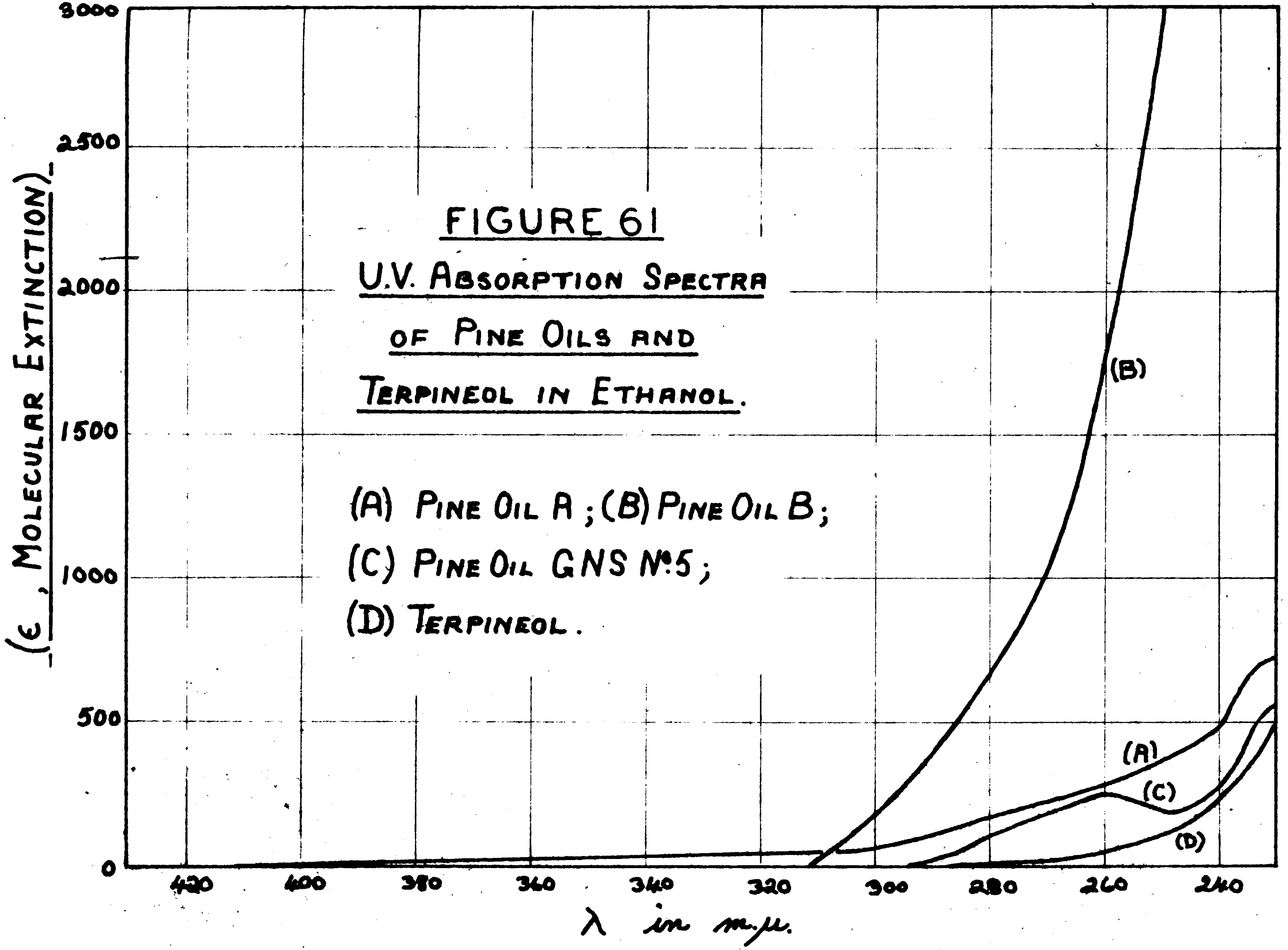


FIGURE 61

U.V. ABSORPTION SPECTRA OF PINE OILS AND TERPINEOL IN ETHANOL.

(A) PINE OIL A ; (B) PINE OIL B ;
(C) PINE OIL GNS Nº5 ;
(D) TERPINEOL .

these substances their molecular weight was taken to be that of their major constituent, Terpineol, i.e. 154 gms. The absorption curve (D) for Terpineol, itself, is also given in the figure. It was obtained from a 0.888 gms./litre solution in Ethanol using a 4 cm. cell.

A study of the curves shows that pure Terpineol gives the lowest extinction values of the group. G.N.S. No. 5 follows Pine Oil A at higher wavelengths, and approaches the Terpineol curve at lower wavelengths. It has a low peak at about 259 mμ not shown by any of the other materials. Pine Oil B gives the greatest extinction values, these being about four times the value, at any given wavelength, given by the other materials. It is suggested that the high values given by Pine Oil B are primarily due to partial polymerisation of the terpenes. Pure terpineol is water white, Pine Oils A and G.N.S. No. 5 had a yellowish tinge, and Pine Oil B had a deep yellow colour. It is thought that the various shades of colour indicate progressive polymerisation of the terpenes in the oil and that various grades of Pine Oil will therefore give absorption curves ranging from that of pure terpineol as the lower limit to the upper limit approached by Pine Oil B.

These factors again indicate that Pine Oil A is somewhat similar to G.N.S. No. 5 while B is materially different.

Froth Stability of Pine Oil Solutions.

The technique employed with solutions of the monohydric alcohols and fatty acids was now utilised to study the froth stability of solutions of the Pine Oils in water.

Frothing Apparatus No. 5 was used for these tests.

Since, to obtain results with these frothers, it is necessary to use much lower concentrations than in the case of the alcohols, a micropipette was constructed which delivered drops of oil of known and constant weight.

e.g. Each drop of G.N.S. No. 5 = 0.010 gms.

Each drop of Frother 60 = 0.009 gms.

Such a pipette made it unnecessary to use large quantities of water to reach the necessary dilutions, since one drop of Pine Oil G.N.S. No. 5 per litre of water is equivalent to a concentration of 10 parts per million of water.

The solutions were made up in carefully cleaned, half litre, glass bottles with ground stoppers. The water used was double distilled and condensed on Pyrex glass. All contamination was avoided in the preparation of the solutions.

The results were more difficult to obtain than in the case of the alcohols, and some modifications in method were necessary. This was largely due to the fact that these oils are not simple substances and contain proportions of insoluble material.....insoluble even at the higher dilutions. For the first of the curves, that of G.N.S. No. 5, over thirty different solutions had to be prepared before it was complete. Although it was found that Pine Oil formed quite a stable emulsion with water, care was taken to shake each "solution" before taking a sample for test. It was necessary also to clean the frothing tube with Chromic Acid after each solution was tested to remove insoluble oil adhering to the glass walls. In the case of the alcohols as stated already the method of testing had simply consisted in adding a volume of solution to the frothing apparatus; raising the rate of air flow to the fixed values; and determining the equilibrium height of froth after the liquid had reached the temperature of the apparatus (25°C). In the case of these "insoluble" frothers, however, there was a falling off in froth height with time of frothing. This was comparatively small in the case of Pine Oil G.N.S. No. 5 and Pine Oil A but quite marked for solutions of Pine Oil B and Frother 60. It was thought to be due to the collection of insoluble oil at the top of the froth, resulting in local lowerings of Surface Tension with corresponding increase in speed of bubble collapse and loss in froth height. After some time, however, the froth column reached equilibrium.

Method.

The clean frothing tube was rinsed with a little of the solution to be tested, the rinsings drawn to waste, and twenty c.cs. solution placed in the frothing tube. The air flow rate was then raised to some convenient value and held there for five minutes, until the solution reached the operating temperature. The air flow was dropped and the froth allowed to collapse, then the air flow was brought up to the predetermined fixed value and the froth height read off on the scale every half-minute until it became constant at the point of dynamic equilibrium. This was taken as the froth height for the solution. This was repeated on the same solution as a check before running it to waste.

The predetermined fixed rate of air flow was Rate No. 3 as given in Table XV and corresponded to 6.0 cms. of water gauge on the flowmeter manometer.

The results of these frothing tests are shown in Figure 62 where the Froth Height/Concentration curves are given for the four frothing agents tested. The results for G.N.S. No. 5 and Pine Oil A are very similar at lower concentrations, and Pine Oil A has greater stabilities at higher concentrations. Both reagents have a maximum froth stability at 500-600 mgm./litre. Neither Pine Oil B nor Frother 60 show a maximum within the range tested. The shape of the Frother 60 curve is essentially different from the others, being almost linear in the range tested. Further tests seem to indicate that a maximum value lies between 1 and 2 gms./litre, but the large quantities of insoluble oil in the frothing tube at these concentrations make it difficult to get consistent results.

The concentration ranges covered for these reagents

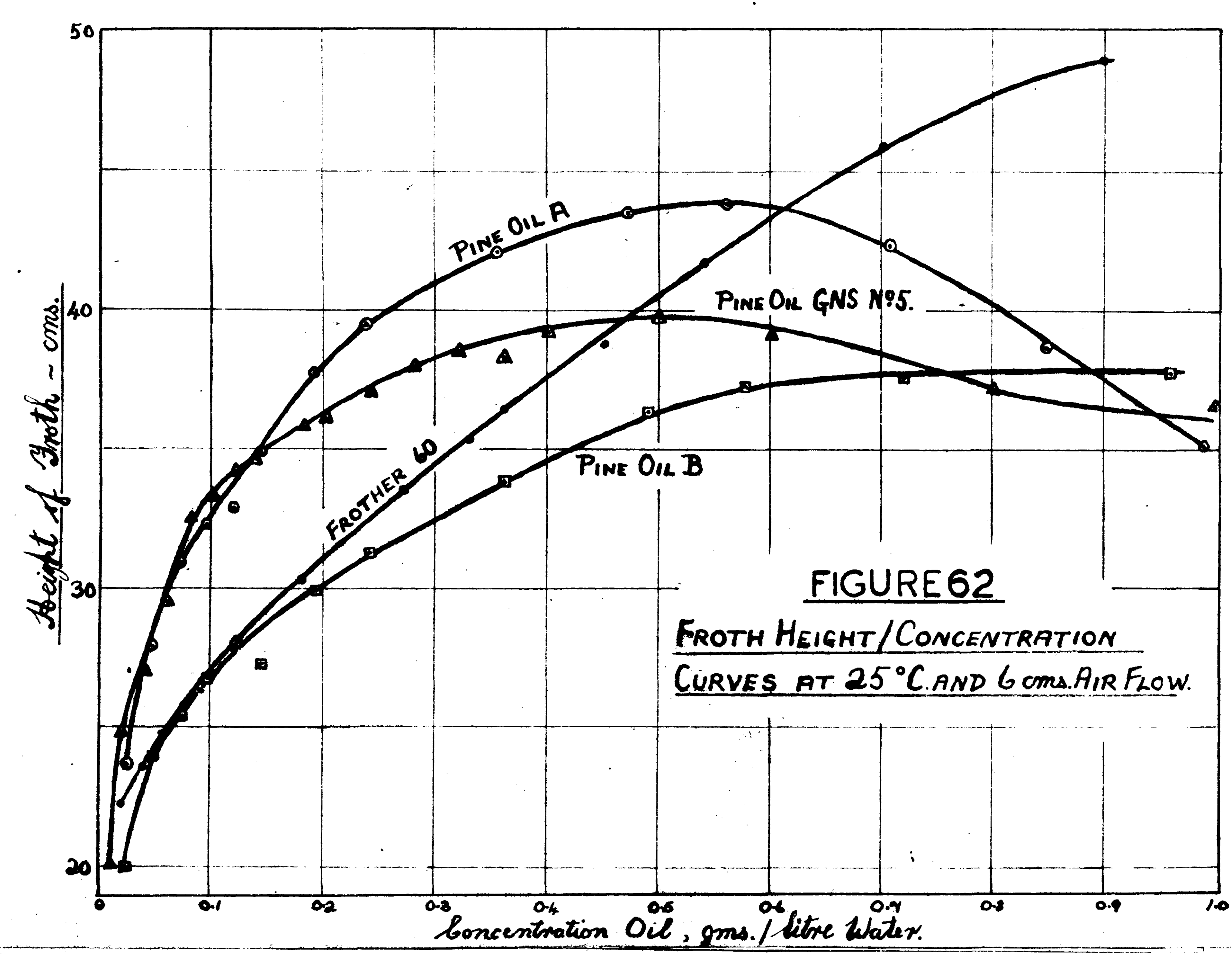


FIGURE 62

FROTH HEIGHT/CONCENTRATION CURVES AT 25°C. AND 6 cms. AIR FLOW.

(up to 1 gm/litre) of course far exceeds that used in practice. The maximum concentration of Pine Oil (G.N.S. No. 5) used as a frother is generally 0.2 lb. per ton of ore, and for Frother 60 the maximum is 0.5 lb. per ton. In an ore pulp of 20% solids this is equivalent to a concentration for Pine Oil of 22.4 mgm./litre water, and for Frother 60 of 56 mgm./litre water.

Froth Stability of Solutions of Pine Oil Components.

In the light of the little information available on the frothing properties of the components of Pine Oil it was decided to carry out a series of systematic frothing tests on solutions of various pine oil components.

Instead of testing all the known components it was decided to test only the major ones, and the materials chosen for test were those that could readily be obtained pure and were easily available in the laboratory.

These chosen in each class were:-

(a) The Secondary Alcohols, Borneol and Fenchyl Alcohol.
(b) The Tertiary Alcohol, α-Terpineol.
(c) The Ketone, Camphor.
(d) The Methyl Ether, Anethole.
(e) The Hydrocarbon, Dipentene.

The preparation of standard solutions of such substances in water is made difficult by their low solubility, and to the fact, as stated by Rhode (68), that the term "solubility" in the strict physical sense is a somewhat loose conception when dealing with compounds of this type. The ease with which they form emulsions with water tends to cause the purely molecular and colloidal regions to merge into one another.

Frothing Properties of Solutions of Borneol, Fenchyl Alcohol, and Camphor.

Pure samples of Borneol and Camphor were prepared by repeated crystallisation of the laboratory grade materials from aqueous Ethanol, and vacuum dried. Fenchyl alcohol was purified by vacuum distillation. The distillate was cooled in a freezing mixture and the crystals filtered off and dried. M.P. = 38°C. Saturated solutions of each of these substances were prepared by shaking excess of the purified materials in double distilled water for 48 hours.

The solubility of Borneol in water at 15°C was taken from the work of Mitchell (69) to be 0.697 gm. per 1000 c.cs. water, and the solubility of Camphor from the work of Rhode to be 1.70 gms. per 1000 c.cs. water. The solubility of Fenchyl Alcohol was taken to be the value given by Wright (70), i.e. 1.30 gms. per 1000 c.cs. water.

Frothing Apparatus No. 5 was used in all the tests. The various solutions used were prepared by diluting the required quantity of the saturated solution with distilled water. 20 c.cs. of solution were used per test and frothing was carried out in the usual way at 25°C. The froth heights were measured at two separate rates of air flow. These were:-

1. 6 cms. water gauge (the rate of flow already used for the Pine Oils).
2. 4 cms. water gauge, equivalent to 2.86 litres/hr at 25°C. This latter rate was used in case any solutions were found that could not be kept in the tube at the higher flow rate.

The froth height/concentration curves for Borneol solutions in water are shown in Figure 63. It can be seen

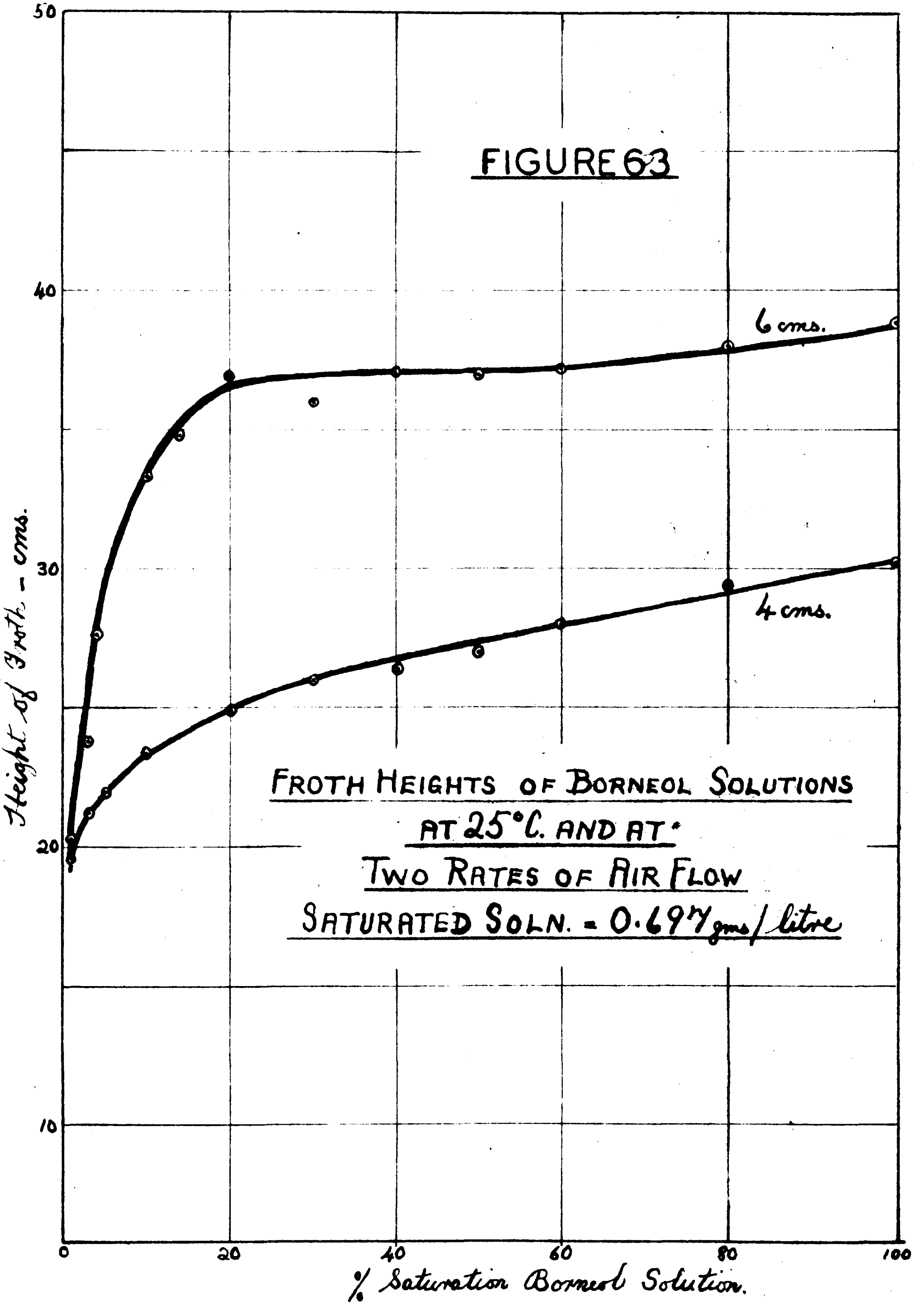


FIGURE 63

FROTH HEIGHTS OF BORNEOL SOLUTIONS AT 25°C. AND AT TWO RATES OF AIR FLOW

SATURATED SOLN. = 0.697 gms/litre

that the curves, unlike those obtained with earlier frothing agents, have no maximum. It was at first thought that this was due to the fact that we had not been using a completely saturated solution, but no significant change in the shape of the curve could be detected using solutions prepared from a saturated solution which had been in contact with solid Borneol for a much longer period than 48 hours. It was noted that if solutions of Borneol more than 50% saturated were frothed for any length of time, solid crystalline Borneol separated from the surface of the froth. This is caused by the rapid changes of surface area taking place at this point causing the solubility to be locally exceeded. This separation of solid material may stabilize the froth at the higher concentrations. No particular difficulty was encountered with the solutions of Fenchyl Alcohol. With solutions near saturation point measurements were made quickly to avoid precipitation in the froth. The greatest froth heights were given by the 50% saturated solution. The curves for the two air-flow rates are plotted in Figure 64.

In the case of Camphor the estimation of froth heights of solutions more than 50% saturated was attended by the same difficulty as was met with in solutions of Borneol. It was felt that the changes in concentration would effect the accuracy of the results, so dilutions of four separate saturated solutions were so frothed and the mean curves from the four sets of results are given in Figure 65. It can be

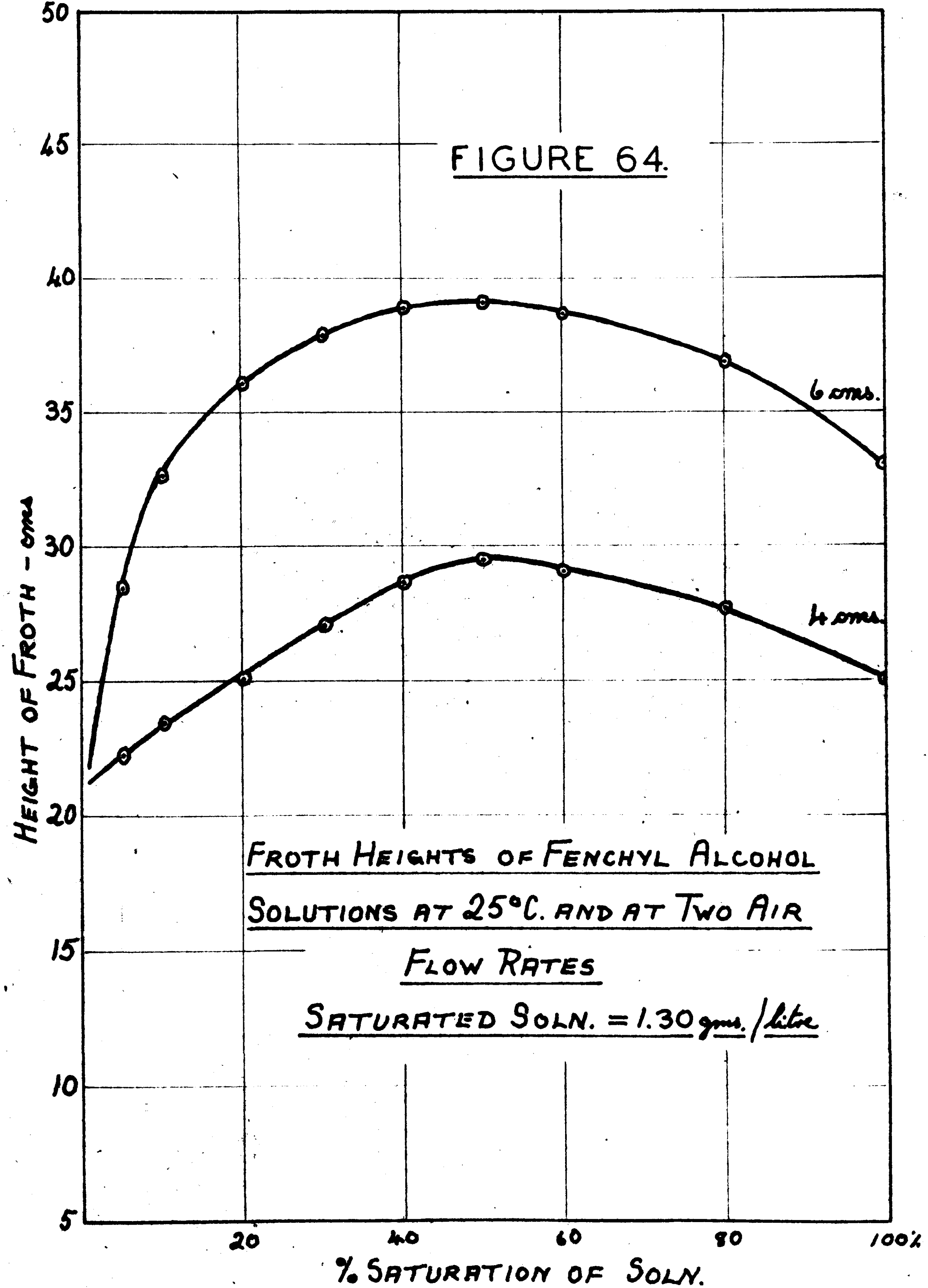


FIGURE 64.

FROTH HEIGHTS OF FENCHYL ALCOHOL SOLUTIONS AT 25°C. AND AT TWO AIR FLOW RATES

SATURATED SOLN. = 1.30 gms./litre

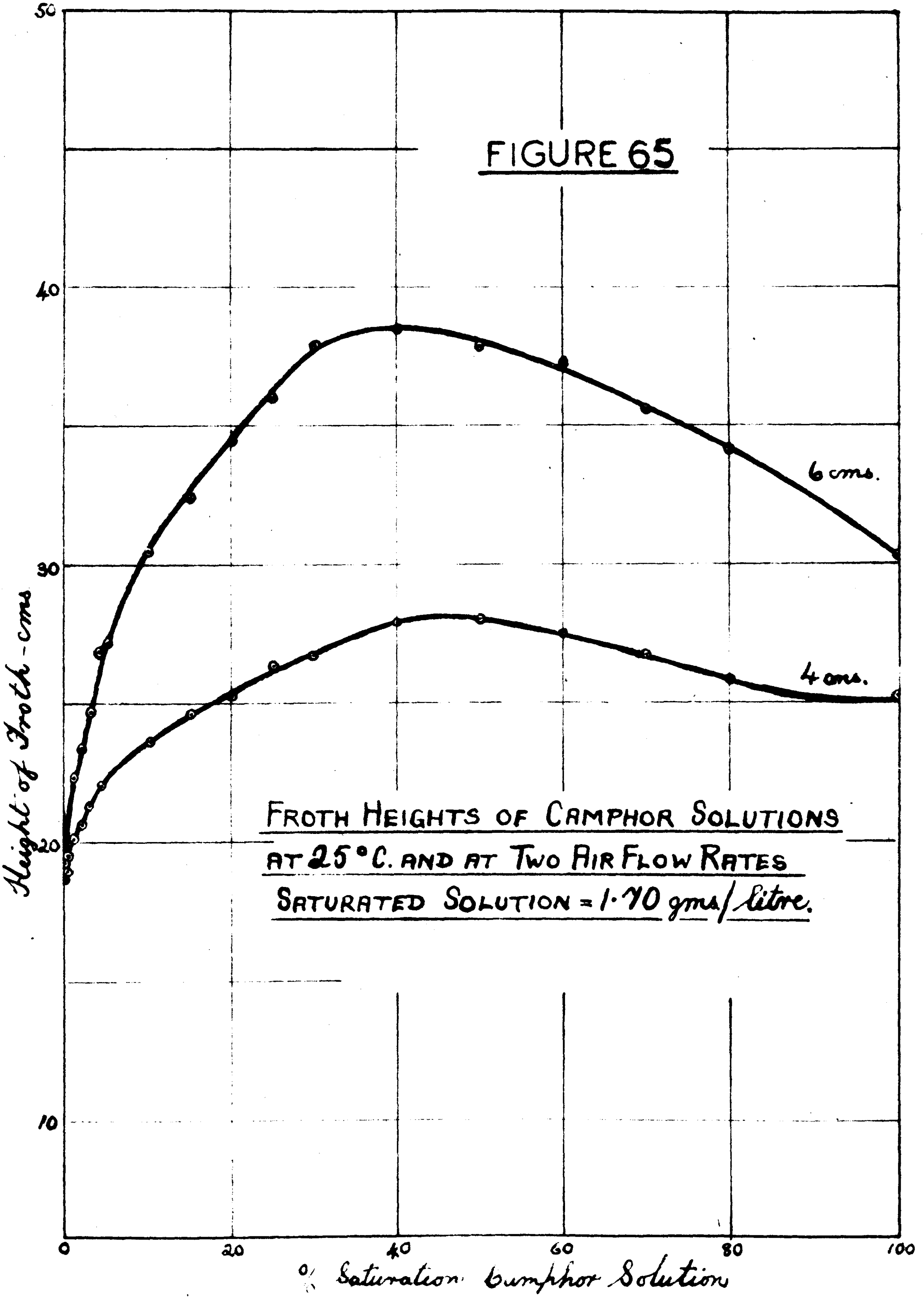


FIGURE 65

FROTH HEIGHTS OF CAMPHOR SOLUTIONS AT 25 °C. AND AT TWO AIR FLOW RATES
SATURATED SOLUTION = 1·70 gms/litre.

seen that Camphor gives the curve of a true frother with a maximum stability at about 40-50% saturation.

Adsorption on Surface of Glass Frothing Tube.

As already mentioned it was soon found that it took the froths of such terpene compounds much longer to reach dynamic equilibrium. As an example of this a typical Froth Height/Time Curve for a solution of Camphor in water is given (Figure 66). The curve shows how the froth height changes from the beginning of the flow of air to the reaching of equilibrium. This rapid change in froth height is not due to the solution coming to the temperature of the apparatus, since the same curve can be obtained again and again by merely stopping and restarting the air flow.

Another new phenomenon soon became obvious. After cleaning the frothing tube thoroughly with Chromic Acid, frothing of a certain solution of Camphor was carried out, and the froth height recorded with time as above. This was repeated three times for the same sample of solution and the results found are plotted in Figure 67. It can be seen that with each successive frothing the froth height became progressively less. The first explanation that springs to the mind is that this is merely caused by the evaporation of the Camphor. But on repeating the test with a new solution of Camphor in the frothing tube (without again cleaning with Chromic Acid) it was found that equilibrium was reached at the second period of frothing. This is best shown by the Table given below.

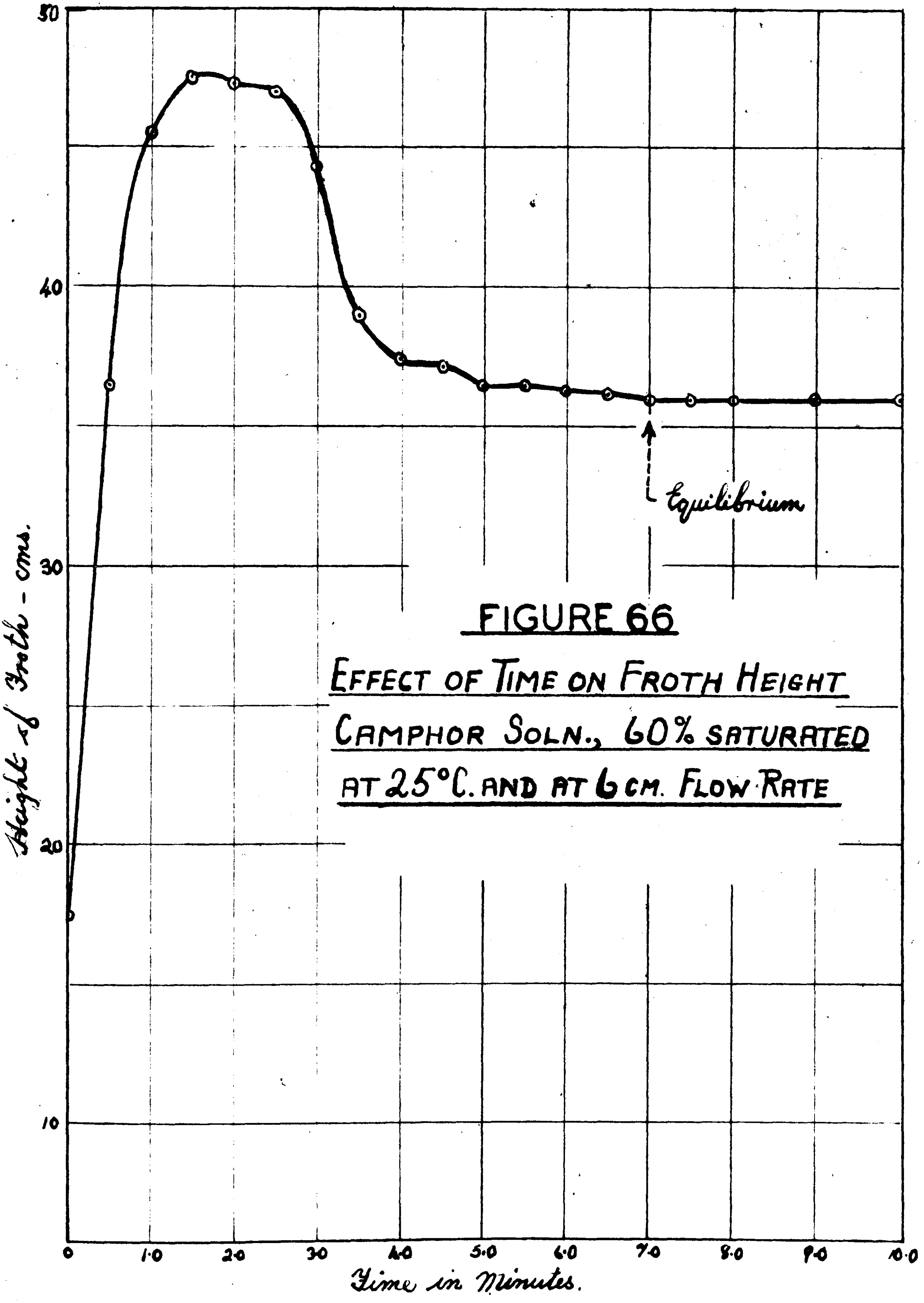


FIGURE 66

EFFECT OF TIME ON FROTH HEIGHT
CAMPHOR SOLN., 60% SATURATED
AT 25°C. AND AT 6 CM. FLOW RATE

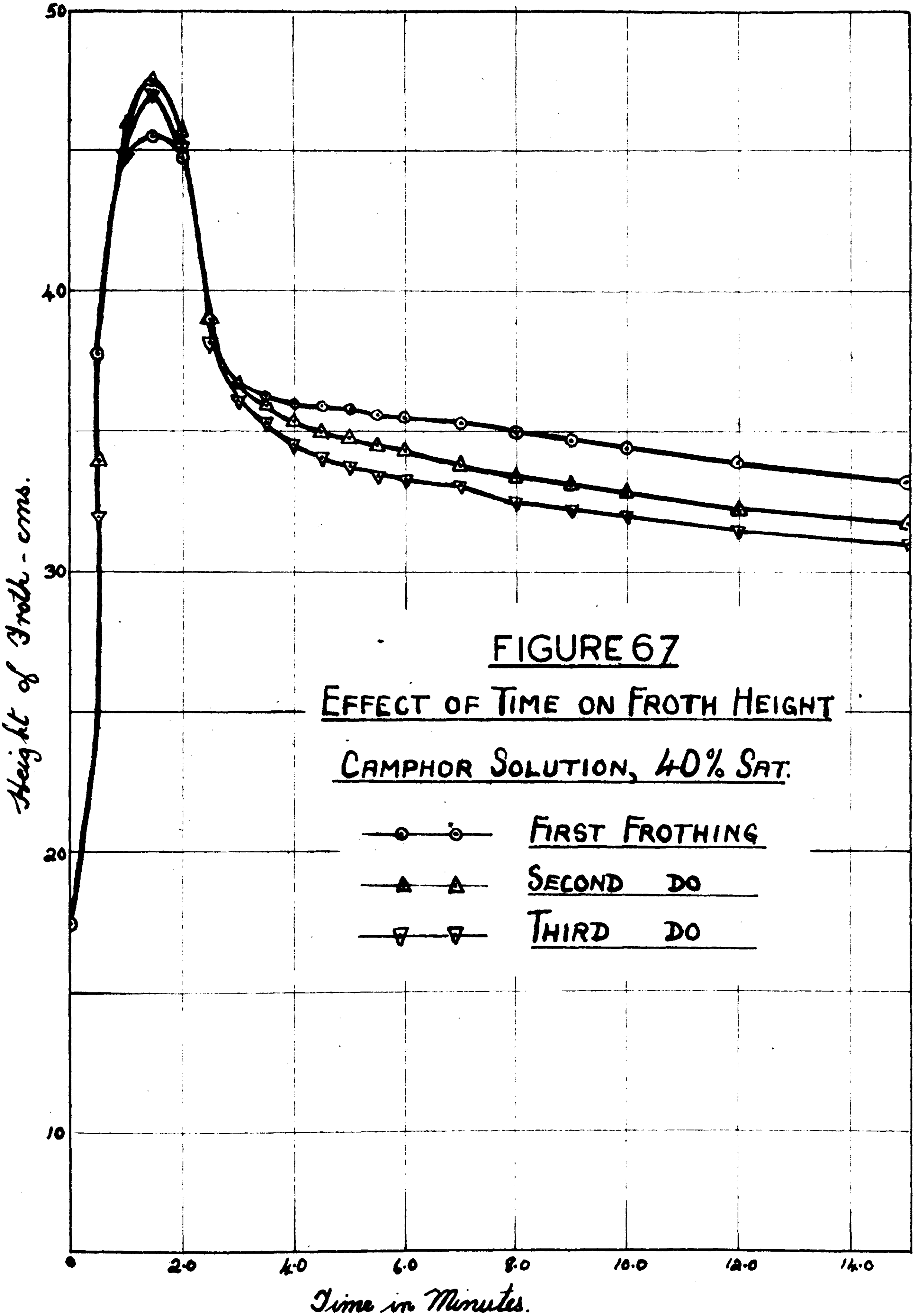


FIGURE 67

EFFECT OF TIME ON FROTH HEIGHT

CAMPHOR SOLUTION, 40% SAT.

Table XXVIII.

Three successive frothing tests on a sample of a 60% saturated solution of Camphor in water. Frothing carried out at a constant rate of air flow equivalent to a flowmeter reading of 4 cms. water gauge.

Time in Mins.	Frothing Tests.		
	(1)	(2)	(3)
0	-	-	-
0.5	36.2	26.8	28.1
1.0	40.5	27.3	27.1
1.5	32.5	26.7	26.6
2.0	30.8	26.6	26.4
2.5	29.9	26.5	26.2
3.0	28.8	26.4	26.2
3.5	27.3	26.3	26.2
4.0	27.3	26.2	26.1
4.5	27.1	26.1	26.1
5.0	27.0	26.1	26.1
5.5	26.8	26.2	26.1
6.0	26.7	26.1	26.1
6.5	26.7	26.1	26.1
7.0	26.7	26.1	26.1
8.0	26.6	26.1	26.1
9.0	26.6	26.2	26.1
10.0	26.5	26.1	26.2
15.0	26.0	26.1	26.1

It can be seen from the table that equilibrium was not reached at all in the first frothing, but in the second it was reached after about four minutes, and in the third after about three minutes. Samples of later solutions reached equilibrium at the first frothing. It seems that this can only be explained by assuming that the freshly cleaned glass wall of the frothing tube was removing Camphor from solution in successive frothings (as in Figure 67) until the glass was saturated. This was verified by cleaning the tube again with Chromic Acid when the phenomenon was again evident. Although this adsorption may be peculiar to Camphor, precautions were taken in later tests to saturate the tube with a suitable solution each time it was cleaned with Chromic Acid. This adsorption has only made itself felt due to the small weights of material involved in the frothing tests of these terpene derivatives. In the tests with previous substances (alcohols and acids) the weight of material to saturate the glass would not be sufficient to markedly change the bulk concentration of frothing agent.

Frothing Properties of Solutions of α-Terpineol.

A sample of α-Terpineol was dried over anhydrous Sodium Sulphate and purified by vacuum distillation; the solidified material melted at 35°C. A saturated solution of this material was prepared by shaking in distilled water at room temperature for 48 hrs. The saturated solution was separated from undissolved material and finally clarified with "Hyflo" celite.

Frothing tests were carried out in the usual way in the No. 5 apparatus. It was immediately evident that the frothing properties of Terpineol solutions far exceeded those of the previous tested constituents. The "8 cm." rate of air flow gave measurable froth heights only at the lowest concentration values. At the higher concentrations the froth came out the top of the apparatus, or was generally above the critical froth height so that large bubbles were formed and results were impossible to obtain.

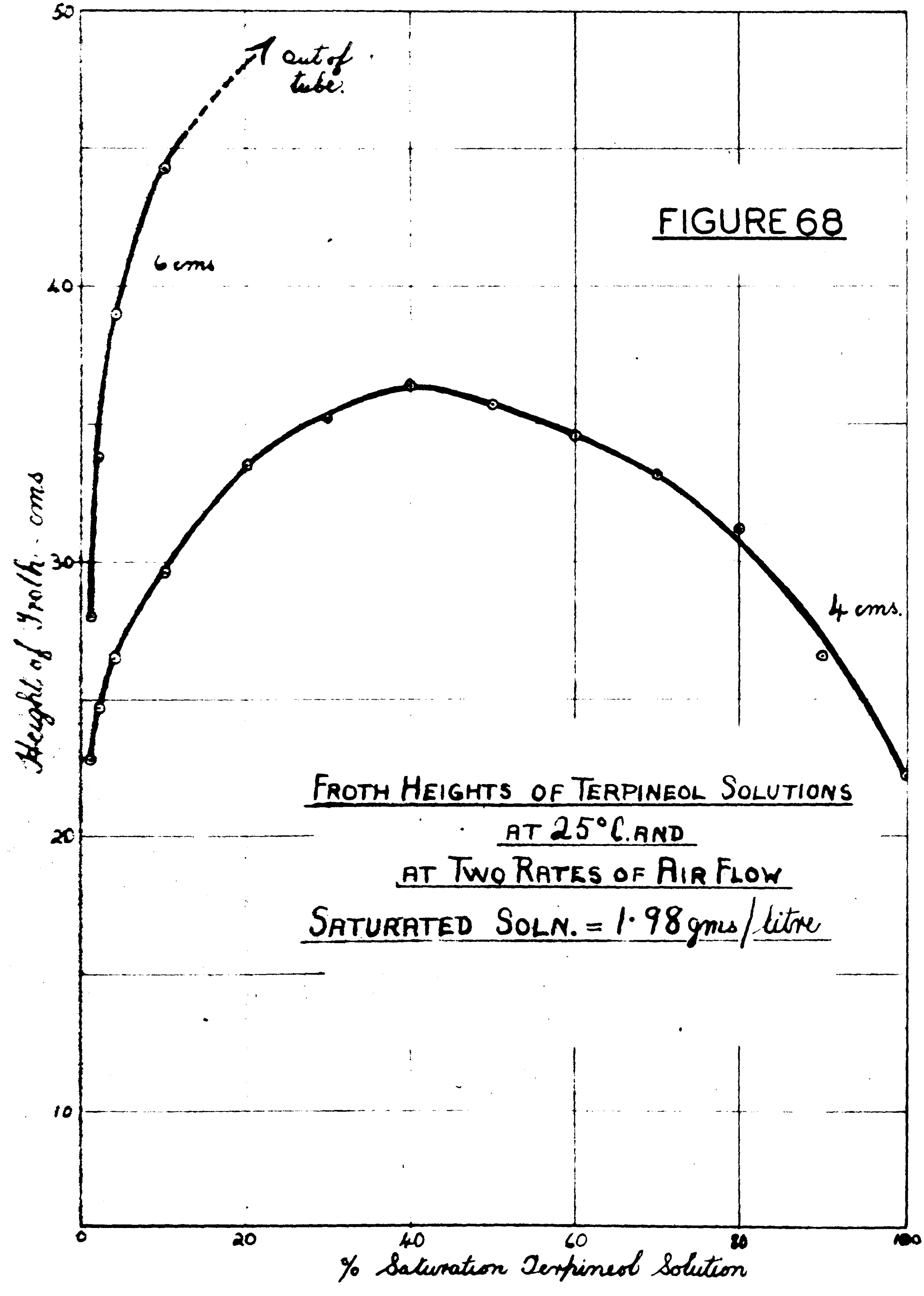


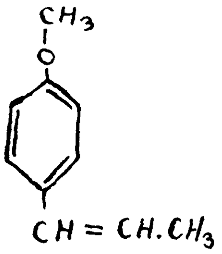
FIGURE 68

FROTH HEIGHTS OF TERPINEOL SOLUTIONS
AT 25°C. AND
AT TWO RATES OF AIR FLOW
SATURATED SOLN. = 1·98 gms/litre

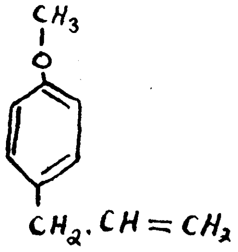
We must therefore revert to the "4 cm." air flow rate curve for comparison with the other Pine Oil constituents. The curves are shown in Figure 68. It can be seen that like Camphor there is a typical "frother" maximum at about 40% saturation.

Frothing Properties of Solutions of Anethole.

Anethole and Methyl Chavicol (Estragole) are the isomeric methyl ethers contained in small proportions in Pine Oil.



Anethole



Methyl Chavicol
(Estragole)

Since the only difference in the two structures is the position of the double bond in the side chain, one would expect their frothing properties to be very similar. This double bond and the ether oxygen atom at the other end of the molecule should make it fairly surface-active. No figures could be found in the literature for the solubility of these materials in water. Anethole is merely classed as being "very slightly soluble" in water and Estragole as "insoluble". Due to the similarity of the structures it was decided to take the frothing properties of Anethole as typifying the ethers in Pine Oil.

The sample of Anethole obtained was frozen and the crystals filtered off. This was repeated until the material gave a Melting Point of 22°C.

A saturated solution of Anethole in water was prepared by the method already described. After the agitation the aqueous phase had to be cleared with repeated quantities of "Hyflo" celite to remove the finely dispersed droplets of undissolved Anethole. Dilutions of the saturated solution were frothed in the usual way and the Froth Height/Concentration curves obtained are given in Figure 69.

It can be seen that the curves do not possess the usual "frother" maximum. In this they are like Borneol, but unlike Borneol we cannot explain the shape in terms of the solid precipitated in the foam.

It has already been found that a normal frother such as, say, Amyl Alcohol gave a curve with a maximum froth stability at an intermediate concentration value. For the materials tested this concentration value corresponded to a constant concentration in the surface film which was much less than that required for a coherent monomolecular layer of surface active molecules and water molecules in a definite ratio. This maximum stability is likely to be associated with the maximum possible difference in concentration between the surface film and bulk of the solution according to the Gibbs' Adsorption Equation. It was also found that saturated or supersaturated solutions of the frother had

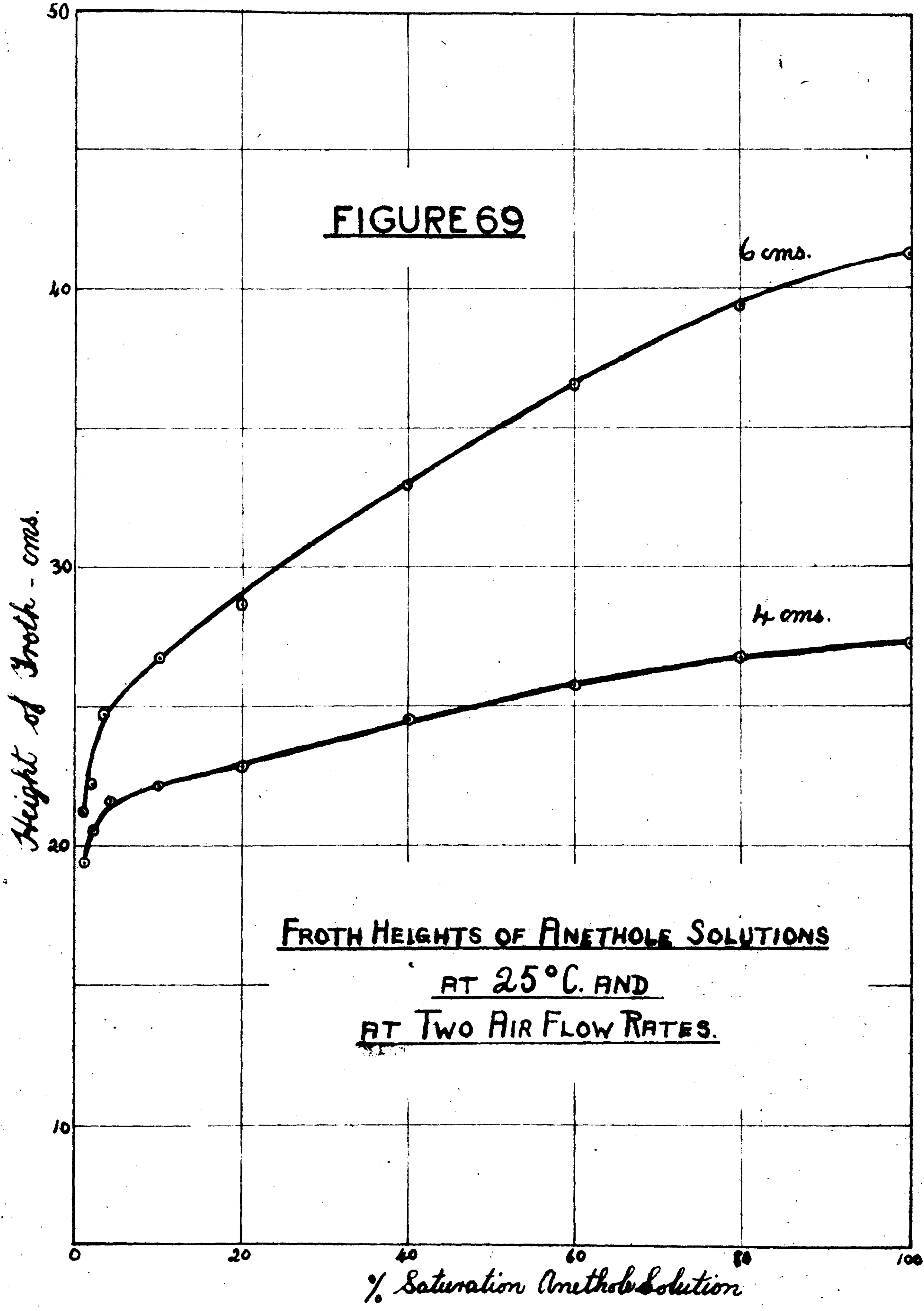


FIGURE 69

FROTH HEIGHTS OF ANETHOLE SOLUTIONS AT 25°C. AND AT TWO AIR FLOW RATES.

little or no frothing power, and that additions of excess liquid frother to a froth already formed by some suitable dilution caused its immediate collapse. These factors were taken as the criteria for a frother.

Now for Anethole there is no maximum at an intermediate dilution; the maximum froth stability occurs at saturation; and the addition of Anethole to the frothing saturated solution did not cause the froth to collapse, if anything it made it a little more stable. We shall thus take these factors as defining a Stabiliser.

Frothing Properties of solutions of Dipentene.

The material obtained was designated "Limonene" and was purified by vacuum distillation. The solution prepared by shaking excess of this material with distilled water remained cloudy even after standing for a week. It was therefore shaken with successive quantities of "Hyflo" celite and filtered until the solution was completely clear. Frothing tests were carried out with this solution in the usual way, and the curves obtained, plotted as in Figure 70. Again it can be seen that the curves have no intermediate maximum. It was also found that the froth height of the saturated solution could be further increased by the addition of quantities of limonene to the solution, showing that the undissolved oil has a stabilizing action on the froth. Although the Limonene seems at first sight to possess all the factors of a stabiliser it seems peculiar that near

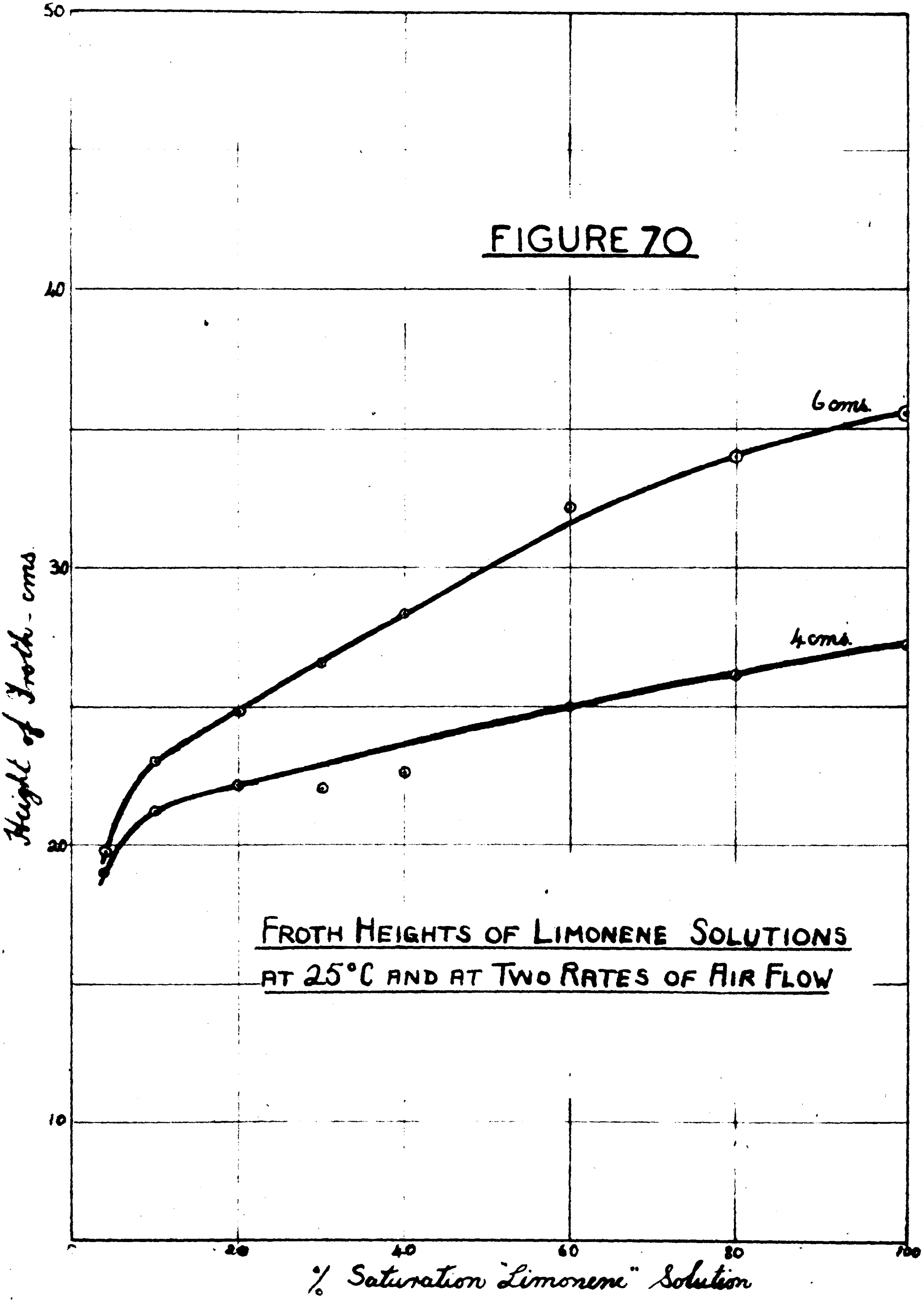


FIGURE 70

FROTH HEIGHTS OF LIMONENE SOLUTIONS AT 25°C AND AT TWO RATES OF AIR FLOW saturation it, a hydrocarbon, should have as large values of froth stability as Borneol, an alcohol.

It was thought that this anomaly might be due to polar impurities in the Limonene, so a new sample was obtained as a check. Since the substance is known to be sensitive to atmospheric oxidation, it was distilled in a current of Nitrogen and the fraction distilling at 176°C collected and stored under Nitrogen. The density and Specific Rotation of this purified material were determined.

Density of distilled "Limonene" $D_{4^\circ}^{20^\circ} = 0.8531$

cf. Density of Limonene (Hbk, Chem. & Phys.) $D_{4^\circ}^{20^\circ} = 0.845$

Specific Rotation of distilled "Limonene" $[\alpha]_D^{20^\circ} = -21,55$

cf. Sp. Rotation of -Limonene $[\alpha]_D^{20^\circ} = 126.84$

Sp. Rotation l-Limonene, (Simonsen, "Terpenes"). $[\alpha]_D^{20^\circ} = -122.6$

The sample must therefore have contained proportions of both isomers, and therefore in spite of its slight rotation shall now be called <u>Dipentene</u>.

The frothing properties of "solutions" containing known quantities of this Dipentene were determined by adding weighed drops of the material to distilled water, shaking for a few minutes, and then frothing 20 c.cs. of each solution in the apparatus. In no case could the solution of the Dipentene be said to be complete and at the high concentrations the "solutions" became quite opaque with suspended drops of undissolved hydrocarbon. The large quantity of undissolved oil in the froth column at the higher concentrations hindered the attainment of equilibrium and in some cases it was nearly 15 mins. before a constant height was reached. The resulting Froth Height/Concentration curves for the two rates of air flow are given in Figure 71. It can be seen that the curves pass through no maximum value.

50 c.cs. of Dipentene were vigorously agitated with 400 c.cs. of distilled water in a closed ½ litre bottle for thirty six hours, then allowed to stand for two days and the phases separated. The separated Dipentene phase was stored under Nitrogen and its Density and Specific Rotation determined.

Density $D^{20°}_{4°}$ = 0.8513

Sp. Rotation $[\alpha]^{20°}_{D}$ = +20.78

These figures seem to indicate that the water had little or no effect on the Dipentene phase.

The frothing properties of the saturated aqueous phase were now tested in the usual way. The froth height/concentration curves are given in Figure 72 These should be compared with Figure 70, which shows the curves obtained for the earlier saturated solution. The new curves show that these solutions can have an even greater froth stability, than was at first thought. Comparison of Figure 72 with Figure 71 should at first sight allow one to calculate the concentration of Dipentene in the saturated solution, since Figure 71 gives froth heights corresponding to known

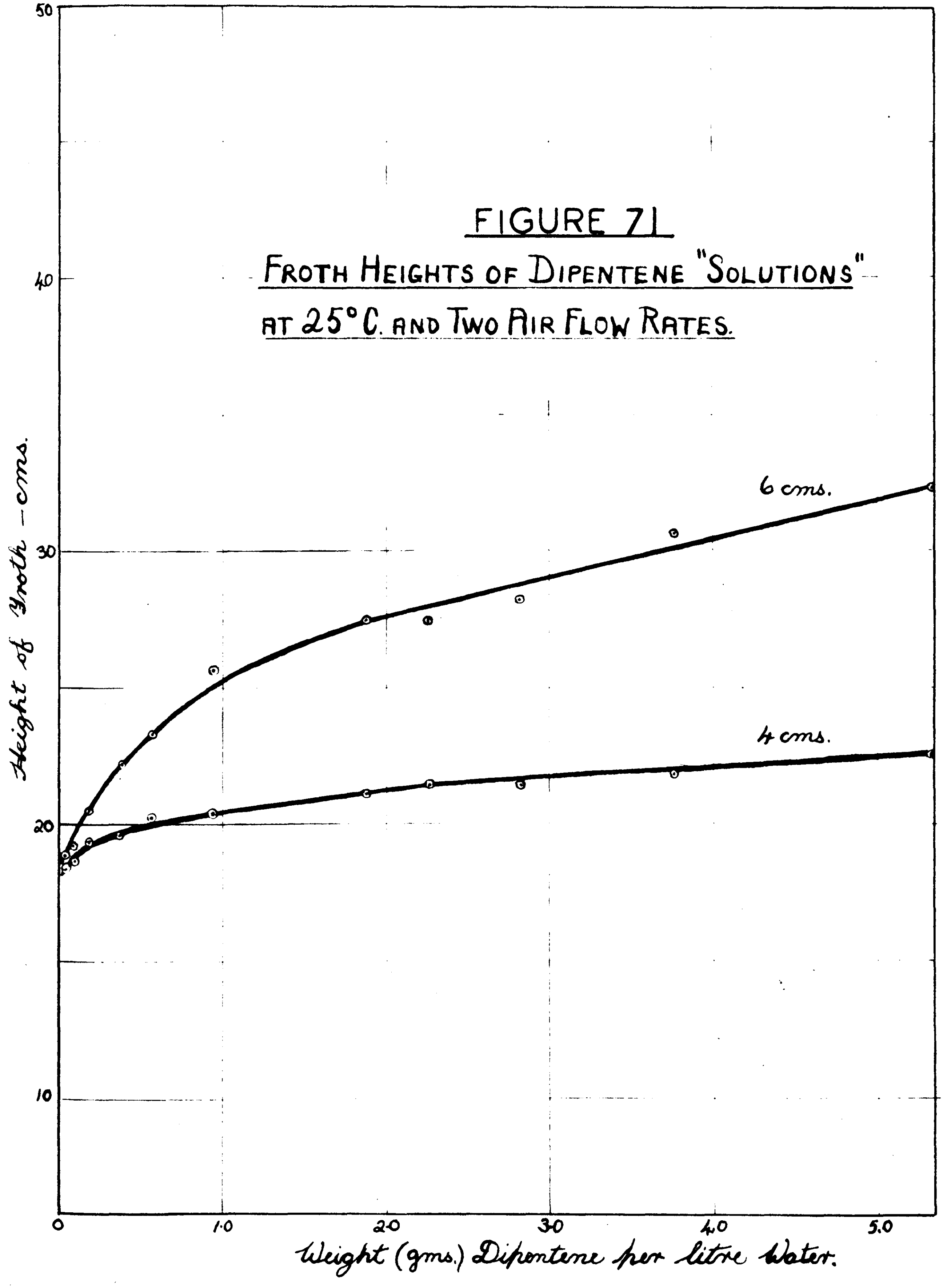
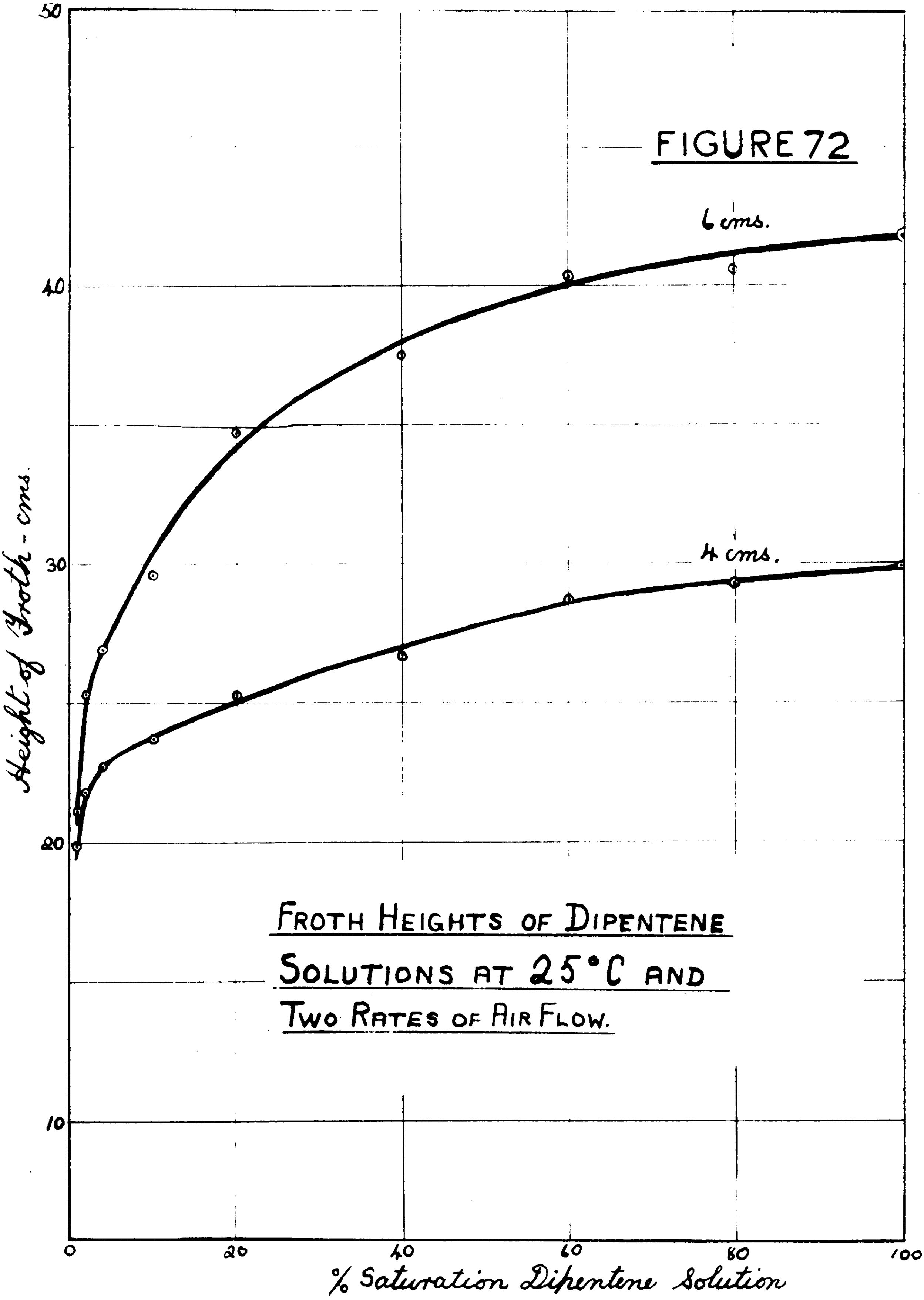


FIGURE 71

FROTH HEIGHTS OF DIPENTENE "SOLUTIONS" AT 25° C. AND TWO AIR FLOW RATES.



FROTH HEIGHTS OF DIPENTENE SOLUTIONS AT 25°C AND TWO RATES OF AIR FLOW.

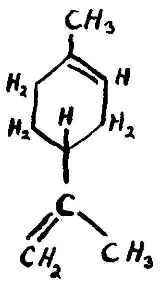
concentrations. But it is seen immediately that the "solutions" of Figure 71, most of which exceed the saturation limit, have a much lower froth stability than those of Figure 72. Since it has already been found that the addition of Dipentene to the saturated solution increases its froth stability, it cannot be said that the low froth stabilities of Figure 71 are due to the undissolved material in the froth lowering the froth stability. A simple qualitative test of frothing of Dipentene/Water mixtures was made by shaking samples in a test tube and it was found that a froth was formed even from a mixture containing equal proportions of Dipentene and Water. It appears therefore that to explain the enhanced froth stabilities of Figures 70 and 72, one must either assume that Dipentene requires prolonged agitation to cause any amount to pass into "solution", or that the material in the aqueous solution is not Dipentene but some reaction product formed between it and water.

By "solution" is meant in this case a dispersion which is more of a colloidal than a molecular nature. The differences in Figures 70-72 would then be due to the different amounts of Dipentene "taken up" by the water in each case. It was found in some cases that clear solutions of Dipentene in water after standing a few days began to shew interference fringes on the surface, indicating that presence of undissolved material - and this in solutions that had been repeatedly cleared with celite. Thus it is obviour that it is very difficult to obtain a solution than can be truthfully said to contain only molecularly dispersed Dipentene.

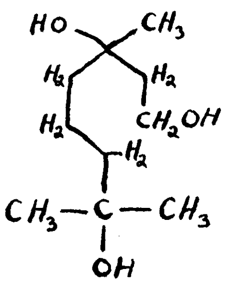
In passing it should be noted that De Witt (67) recorded surface tension measurements on a solution containing 0.753 gms. Dipentene per 1000 c.cs. water. This should be compared with the solubility of Borneol as recorded by Mitchell (69), i.e. 0.697 gms. per 1000 c.cs. water. It hardly seems likely that of two terpene compounds, of roughly similar molecular weights, the hydrocarbon would be more soluble than the alcohol.

There is a chance that Dipentene (I) held in contact with water for some time becomes hydrated to Terpin Hydrate (II). It is known to do this in contact with mineral acid. This transformation may even go as far as Terpineol (III). We have already noted the excellent frothing properties of Terpineol; and (II) from its structure should be as good.

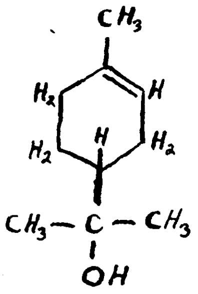
I



II



III



A rough qualitative test of an aqueous solution of Terpin Hydrate showed that it had good frothing properties. The small quantities of material involved will hinder the verification of the above transformation. No rotation could be detected when a sample of the saturated Dipentene solution was viewed by polarised light.

Spectral Study of Dipentene.

It was thought that the conversion to Terpin Hydrate or some similar compound might be detected through the U.V. absorption spectra of the aqueous solutions. This was determined on a sample of the saturated aqueous Dipentene solution, as used in the frothing tests, by means of the spectrograph mentioned earlier. Since the concentration of this solution was unknown it was not possible to plot the molecular extinction coefficient but only the observed extinction (E), i.e. log $\frac{I_o}{I}$. In order to obtain the full range of the curve to the lowest wavelength recorded by the photographic plate, a number of dilutions were made and the extinction values calculated back to that which would have been given by a 1.0 cm. cell and the saturated solution. This is plotted in Figure 73 against wavelength. The curve has no characteristic peaks but indicates a sharp rise to almost complete absorption below about 300 mμ. The absorption spectra of a purified sample of Dipentene in Ethanol (1.074 gm./litre) was also obtained using a 2.0 cm. cell. This is plotted in Figure 74 along with the curve already obtained for

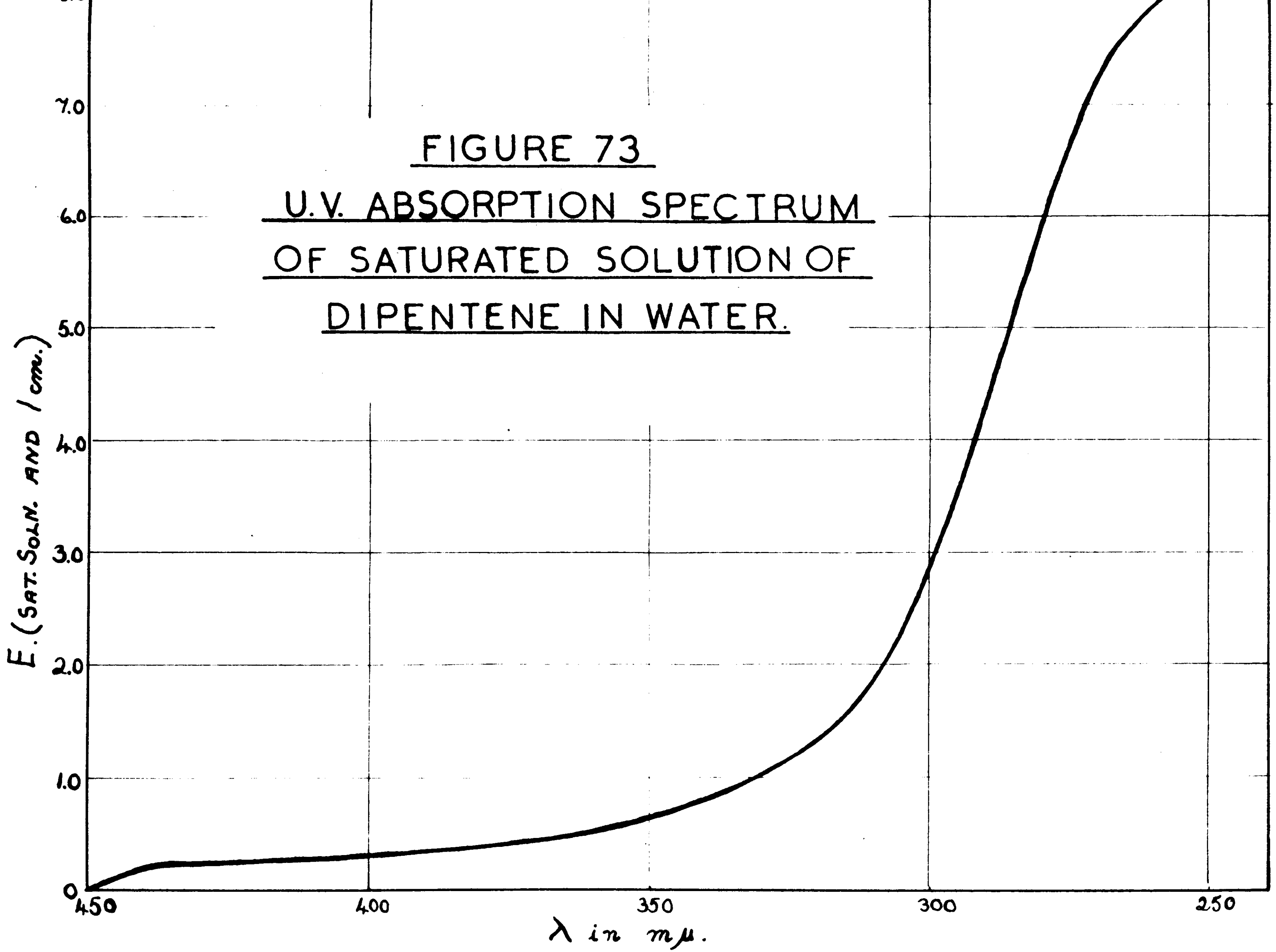


FIGURE 73

U.V. ABSORPTION SPECTRUM OF SATURATED SOLUTION OF DIPENTENE IN WATER.

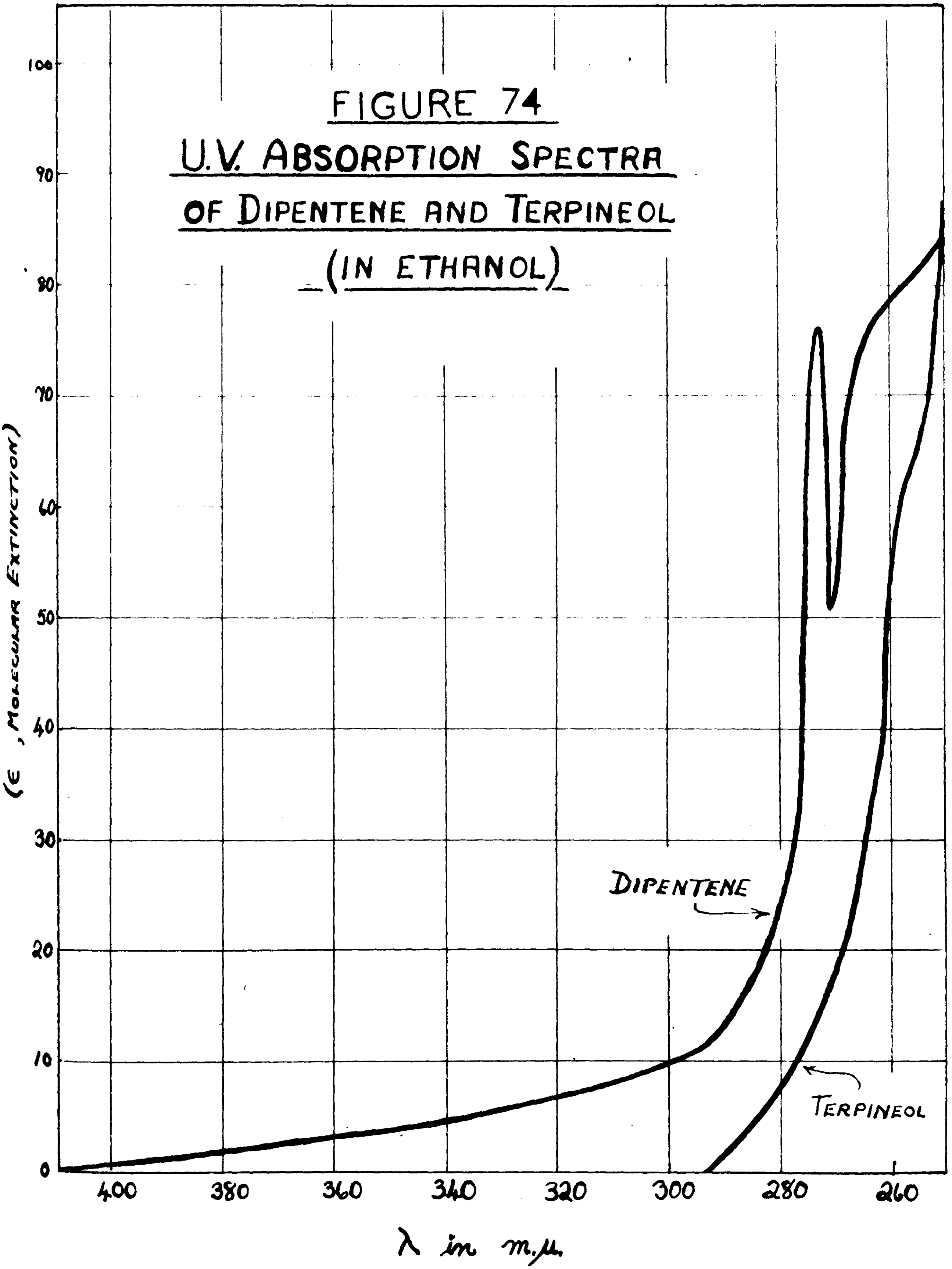


FIGURE 74
U.V. ABSORPTION SPECTRA
OF DIPENTENE AND TERPINEOL
(IN ETHANOL)

Terpineol. While Terpineol shows a sharp rise to almost complete absorption over the range 300 mμ - 250 mμ, the Dipentene sample, although somewhat similar, has an additional narrow band rising to a sharp peak at about 272 mμ. This was not evident in Figure 73. Attempts were made to obtain the absorption spectra for Terpin Hydrate in water but even with a solution of 1.0 gm./litre and a 4.0 cm. cell no absorption could be detected.

At first sight the curve of Figure 73 appears to be more similar to that for Terpineol in Figure 74, in that there is no obvious band formation.

Using the fundamental spectral formula,

i.e. $$\epsilon = \frac{E}{c.d.} \times M$$

where ϵ is the molecular extinction coefficient,

E is the observed extinction,

c is the concentration (gms./litre),

d is the cell length (cms.),

and M is the molecular weight of the substance,

an attempt can be made to make the curve of Figure 73 coincide with the molecular extinction curve for Terpineol in Figure 74.

Thus, for the curves to coincide at 285 mμ, say, there would require to be concentration of Terpineol in the aqueous Dipentene saturate equivalent to

$$c = \frac{5.1 \times 154}{4.5 \times 1.0} = \quad 174 \text{ gms./litre}$$

and at 270 mμ, a concentration equivalent to

$$c = \frac{7.2 \times 154}{19.0 \times 1.0} = \quad 58.4 \text{ gm/litre.}$$

Since these figures are infinitely greater than the solubility of Terpineol in water the curves cannot coincide.

If in the same way one tries to identify the curve of Figure 73 with the lower portion of the Dipentene curve in Figure 74, the concentration in solution from values at 300 mμ is given be

$$c = \frac{2.84 \times 136}{9.7 \times 1.0} = \quad 39.8 \text{ gms/litre.}$$

and at 280 mu

$$c = \frac{5.87 \times 136}{24.0 \times 1.0} = 33.3 \text{ gms./litre.}$$

again impossibly high figures for the solubility of a terpene in water.

It was obvious therefore that the solution of Figure 73 was giving much higher absorption values than the pure materials dissolved in Ethanol. It will be remembered that Pine Oil B (Figure 61) showed high absorption values similar to those of Figure 73, and in that case the anomaly was explained through polymerisation of the terpene content of the oil. This also may be the explanation of the high values of Figure 73, Waterman and Perquin (71) indicate that the terpene Dipentene in presence of air and a diatomaceous substance polymerises readily. Since the saturated "solution" of Dipentene in water used in the frothing tests and spectral study had been repeatedly cleared by agitation with quantities of celite (a diatomaceous material) before use, and no particular care had been taken to exclude air from it, it was quite possible that polymerisation of the small quantity of Dipentene in the aqueous phase had taken place.

A pure sample of Dipentene was refluxed for some hours, until it turned a golden yellow colour. This material was distilled to separate unchanged Dipentene and only the sample distilling above 180°C was collected. The absorption spectra of this material dissolved in Ethanol (0.986 gms/litre) was obtained using a 0.5 cm. cell. The experiments was repeated with a fresh sample of Dipentene which was refluxed until it was a red-brown colour. This was distilled as before, only the sample distilling above 200°C being collected. This was a dark brown viscous resin, and its absorption curve (0.992 gm/litre Ethanol and a 0.5 cm. cell- is given in Figure 75 together with that given by the sample distilling above 180°C. Since the molecular weights of these polymers were not known the extinction coefficient was calculated to a basis of a solution containing 1.0 gm/litre and a 1.0 cm. cell. The absorption curve for pure Dipentene recalculated to this scale is given in Figure 75 for comparison.

Although the polymers do not show the peak at 272 mμ given by pure Dipentene the increase in absorption with polymerisation is at once obvious. As indicated by the darkening in colour of the polymer, the more viscous the material, (i.e. the larger the polymer units) the stronger is the absorption.

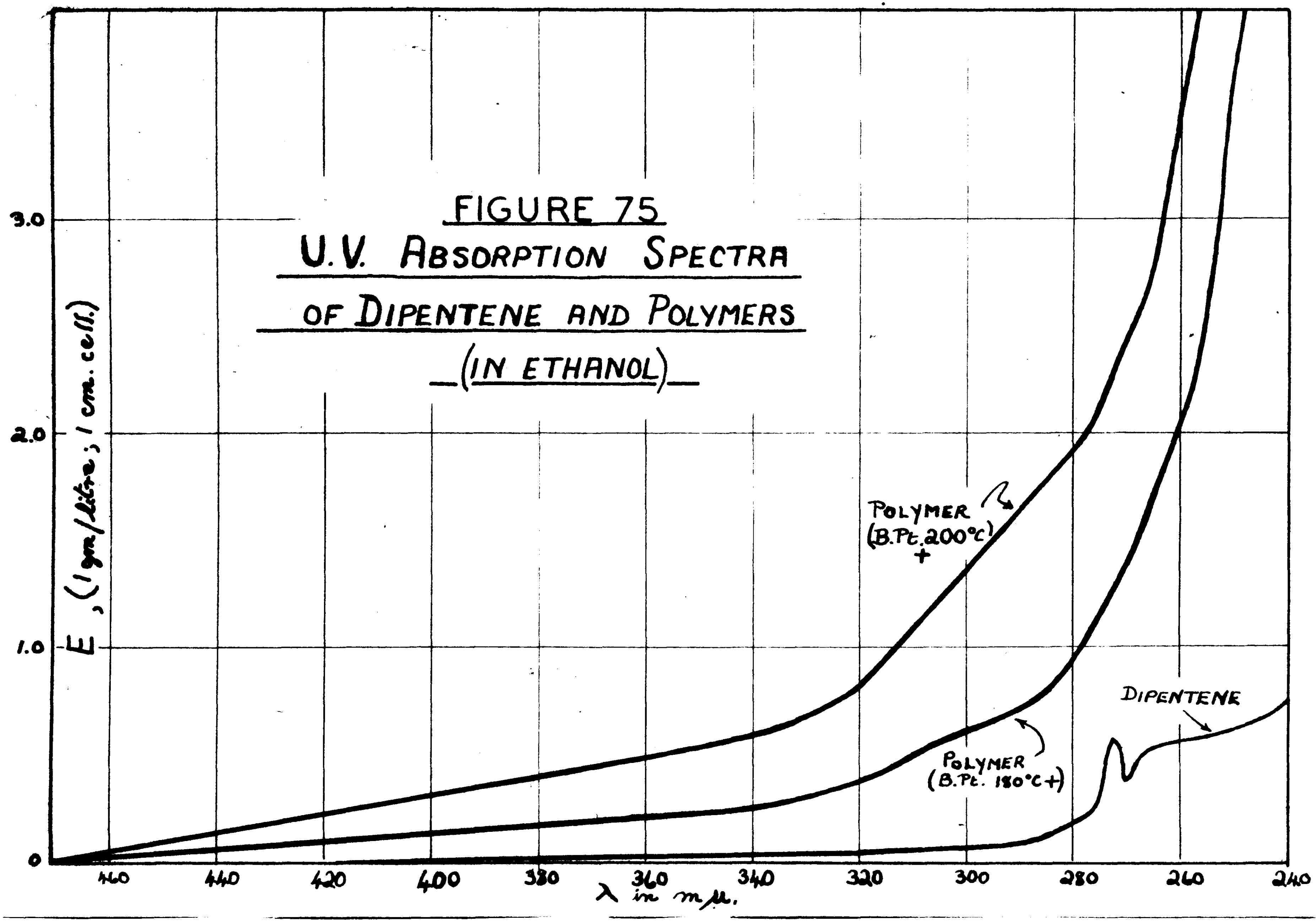


FIGURE 75
U.V. ABSORPTION SPECTRA
OF DIPENTENE AND POLYMERS
(IN ETHANOL)

This study seems to indicate that although the saturated solution of Dipentene in water may contain traces of Terpin Hydrate and Terpineol, it most probably contains polymerised Dipentene. One is unable to calculate the quantity of polymer in solution since the degree of polymerisation is unknown. It seems, however, that the terpene has retained something of its polar properties in the polymerised form to be sufficiently soluble in water to give the ultra violet absorption recorded in Figure 73, and to furnish froths of the stabilities shown.

Theory of Mode of Action of a Stabiliser.

Having discussed the reasons for the froth stability of the saturated solution of Dipentene and the non-stability of the saturated solution of Terpineol, it must now be discovered why it is that excess Dipentene further stabilises its froth and excess Terpineol has no effect. An explanation can be offered in terms of the Spreading Coefficient of the undissolved material on the solution.

For a thin lens of oil to spread on water we must have the relation

$Taw > Tao + Tow$ ....(32)

where

Taw = the surface tension of the water.

Tao = the surface tension of the oil.

Tow = interfacial tension between oil and water.

From this can be developed the Spreading Coefficient,

$S = Taw - (Tao + Tow)$ ....(33)

The interfacial tension and the two surface tensions are now those of the mutually saturated liquids. It can be seen that if S be negative, spreading cannot take place, while if it is positive or zero spreading occurs. Thus one can increase the possibility of spreading by lowering the oil surface tension and the interfacial tension while Taw remains relatively high.

Oleic acid placed on water first spreads then contracts into lenses. This is due to the fact that at first the water Surface Tension is high enough to balance out the other forces but as a monomolecular film of acid forms on the water surface, i.e. it becomes contaminated, the Surface Tension drops and S becomes negative. The spreading on water of paraffin oil containing various "spreaders" has been studied by Heymann & Yoffe (72). These "spreaders" are substances which greatly reduce the interfacial tension between water and oil without greatly effecting the Surface Tension of the latter. They contaminate water only slowly so that for the first stage of spreading the Surface Tension of water still has its usual value. As a result the difference Taw - (Tae + Tow) is increased by the "spreader", and spreading occurs. However, they gradually pass from the oil phase into the surface of the water thus reducing the Surface Tension, the difference Taw - (Tae + Tow) becomes negative and the film gathers into lenses.

Now if it is presupposed that Dipentene stabilizes by virtue of the fact that it forms a stable film on the bubble wall, it must fulfil the above relation for spreading. Used alone it has the important advantage that it cannot lower the surface tension of the aqueous phase much. De Witt gives the surface tension of a saturated solution of Dipentene in water at 25°C as 71.5 dynes/cm., thus the value of S will be kept positive and a stable film is formed.

In the case of Terpineol the surface tension of the saturated solution in water is about 38.4 dynes/cm. This is so low that, on the addition of Terpineol to the surface of the saturated solution, S will be negative and no filming will occur. If one adds Terpineol to a froth formed by another frother, or by say a solution of Dipentene - as Dipentene acts as a weak frother below its saturation point, contact with the bubble films locally lowers the Surface tension and the bubbles collapse. This is the same phenomenon observed as when Ether vapour is brought in contact with a soap froth. The terpene alcohol thus dissolved in the solution and with continued aeration is adsorbed at the interfaces formed. Since the energy of a system always tends to a minimum, that compound will be adsorbed most which produces the lowest surface tension. The froth will now take on the characteristics of this compound, i.e. a more stable or less stable froth will be produced.

Thus a frother can be used as a "destabilizer". As an example of this we have the use of amyl alcohol in organic preparative work to destroy frothing produced during distillation, refluxing, evaporation, etc. Here the froth is generally produced by large surface-active molecules in solution which have quite a small effect on the surface tension but produce a very stable froth by virtue of their size. The addition of amyl alcohol causes the large surface active molecules to be displaced from the interface and be replaced by amyl alcohol molecules as the surface tension drops. Any froth now formed will be characteristic of amyl alcohol, and will be negligible at the temperature and concentration used.

The addition of Dipentene to a Terpineol solution froth does not cause its immediate collapse since it will have little effect on the surface tension. New factors, however, come into play. As soon as the Dipentene comes into contact with the solution interface Terpineol begins to pass into the Dipentene phase to satisfy the Partition Coefficient of Terpineol between Dipentene and water. As a result the surface tension of the solution (Taw) rises and the interfacial tension between Dipentene and the solution (Tow) drops. Thus the difference Taw - (Tao + Tow) becomes more positive and a stable film is formed, with an accompanying increase in froth stability.

If we neglect for an instant this stabilizing action, we see the froth will take on the characteristics of the final concentration of frother in the aqueous phase. The stabilizer can therefore play a part in controlling the concentration of the frother in the aqueous phase, and by judicious choice of stabilizer and concentration of frother in it the partition coefficient can be so arranged that it should be possible to obtain any desired concentration of frother in the aqueous phase. It also becomes less possible to add too much reagent, which is liable to happen with a plain frother. Thus apart from its purely stabilizing action the stabilizer makes it possible to work with larger quantities of reagent and to stretch the desirable portion of the frother's stability/concentration characteristics, i.e. zero to maximum froth stability, over a much larger concentration range till it finally becomes almost linear. Of the Pine Oils studied, Pine Oil G.N.S. No. 5 and Pine Oil A contain little stabilizer, and Pine Oil B and Frother 60 contain much. It should be noted that if too much stabilizing hydrocarbon is used the adverse effect of the greatly reduced frother concentration in the aqueous phase whill greatly outweigh the advantageous stabilizing action. This is seen in the reduced frothing power of Pine Oil B. Of course, when solid mineral is also considered in this analysis, other factors such as oiling of the mineral surface have to be weighed up before the final concentration of stabilizer to be used is decided upon.

In Figures 76 and 77 a comparison is made of the Froth Height/Concentration curves of the various reagents tested. The curves are only repeated where the actual concentration of reagent in solution is known.

Stability Constants for Frother Constituents of Pine Oil.

The froth volume stability constant (M) and apparatus constant (N) were determined for 50% saturated solutions of Borneol, Camphor, Fenchyl Alcohol, and Terpineol. This was accomplished in the usual way using 20 ccs. of each solution in frothing apparatus No. 5. The values obtained were:-

	M	N
Borneol	5.86	0.147
Camphor	6.15	0.157
Fenchyl Alcohol	6.39	0.146
Terpineol	6.99	0.118

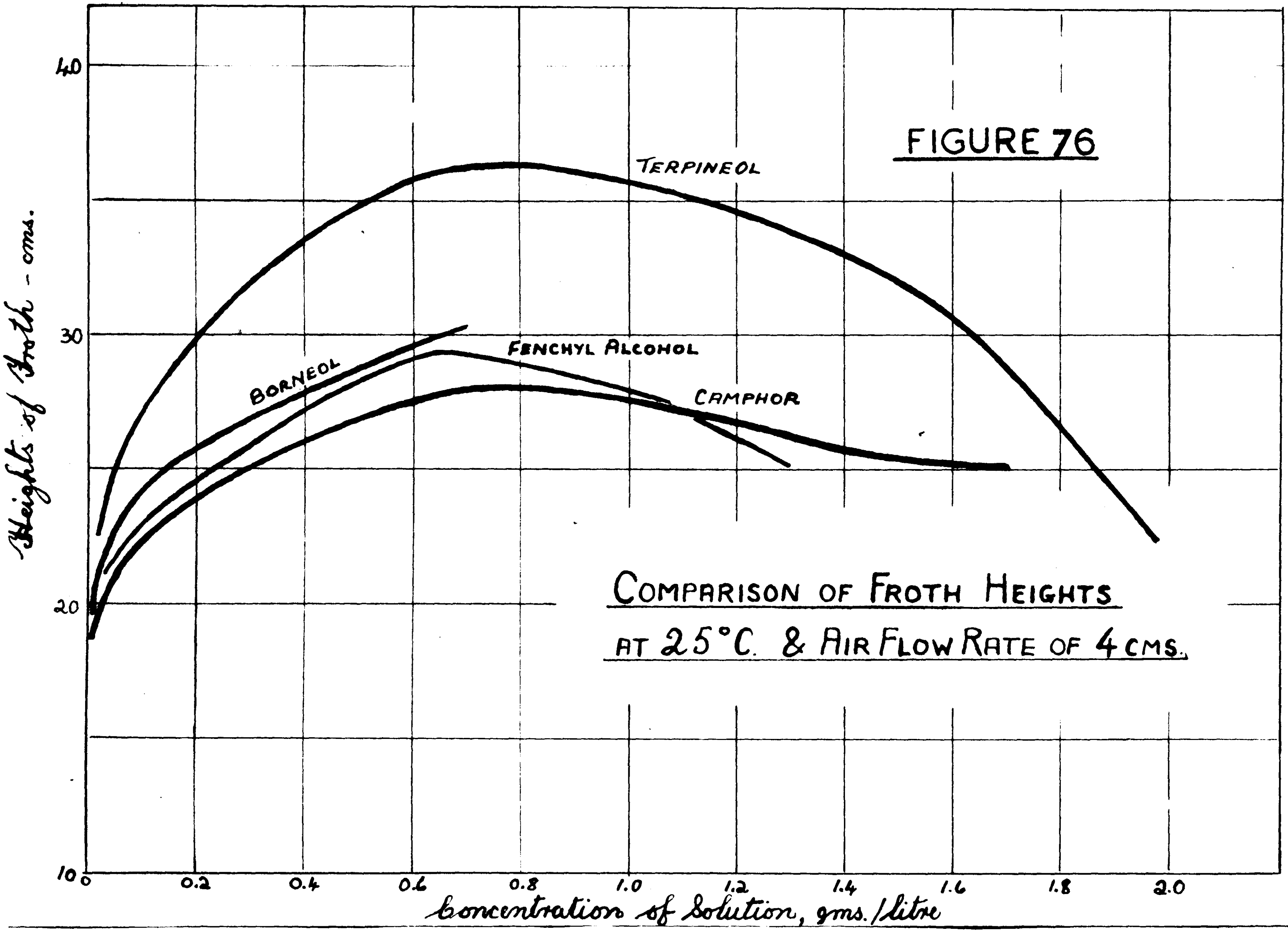


FIGURE 76

COMPARISON OF FROTH HEIGHTS AT 25°C. & AIR FLOW RATE OF 4 CMS.

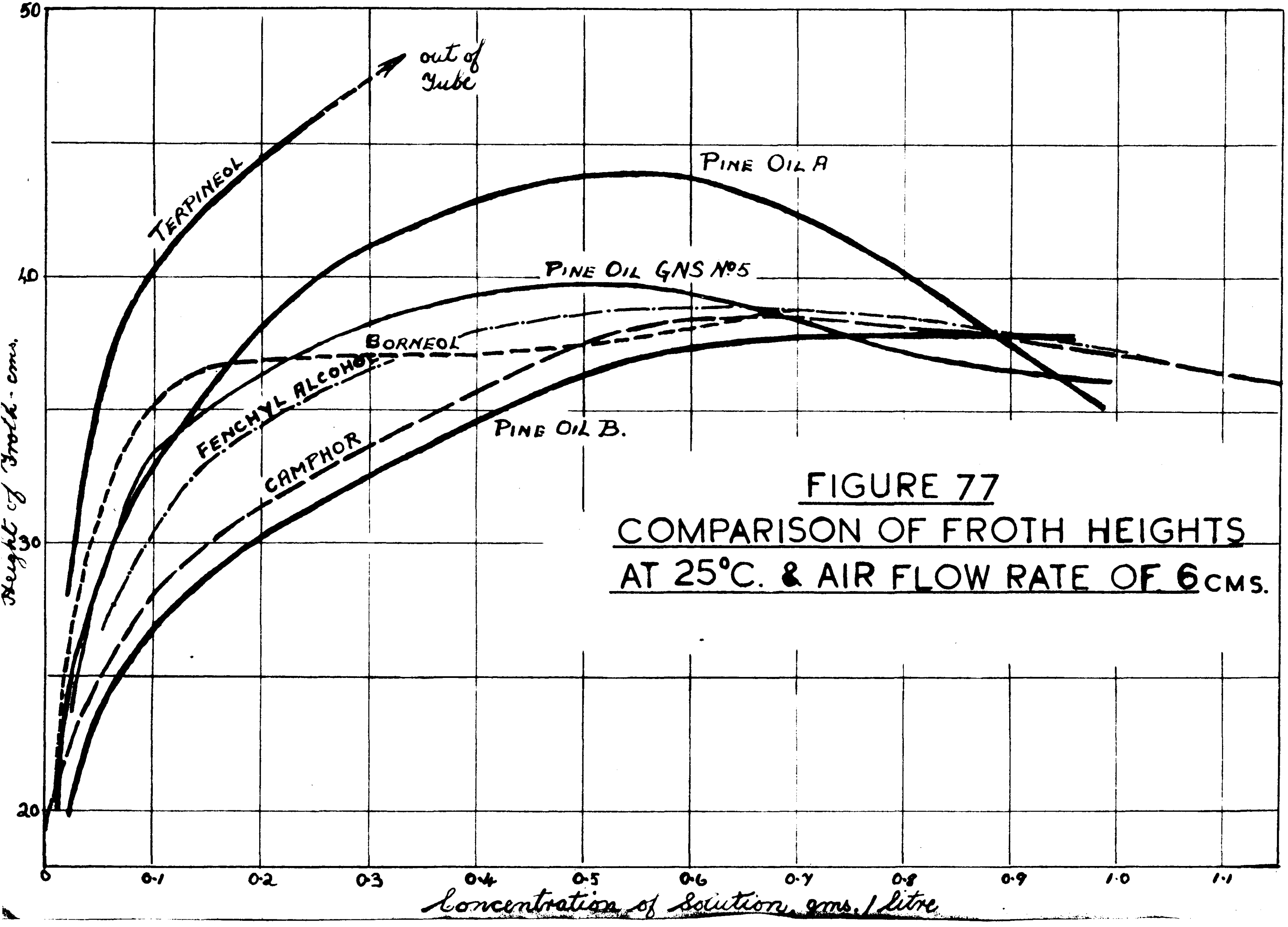


FIGURE 77
COMPARISON OF FROTH HEIGHTS
AT 25°C. & AIR FLOW RATE OF 6 CMS.

These values of M increase in the same order as do the heights of the same solutions shown in Figure 76. These materials can now be compared with the monohydric alcohols, and it can be seen that only n-Heptanol with an M value of 6.17 can compare with these terpene derivatives as a frother. If it is accepted that they have the order of froth stability required for froth flotation, it appears that a frother intended for use in flotation practice should have a value of froth volume stability constant (M), at 50% saturation in water, between 6.0 and 7.0 units (log cc. sec. $cm.^{-1}$)

FLOTATION TESTS WITH PINE OIL AND ITS COMPONENTS.

A standard flotation test was developed from the information gained in the tests already reported in order to compare the properties of the various Pine Oil components.

The feed material for the tests was a Coal/Limestone mixture. About one cwt. of small coal ("washed singles") was rough ground to 20 mesh in a roller mill, then passed through a high speed squirrel-cage grinding unit simultaneously with an equal weight of about 10 mesh Limestone chips, giving an intimately mixed flotation feed containing about 50% Limestone.

The ash content of the original coal was determined prior to mixing with Limestone.

Average ash content of coal = 8.5%.

A sample of the Coal/Limestone feed mixture was screened. The resultant analysis is given below.

Screen Analysis of Feed Mixture.

Sieve	% on Sieve	% Undersize.
16 B.S.S.	3.95	96.05
30 "	15.55	80.50
60 "	18.65	61.85
85 "	10.15	51.70
100 "	5.65	46.05
150 "	10.25	35.80
< 150 "	35.80	-

This feed material was stored in a large, closed, galvanised-iron bin, and before starting each series of flotation tests sufficient feed was withdrawn from the bin to cover the tests and the bin closed. Since each series consisted of about six flotation tests each with 600 gms. feed, about five kilos were taken in each series sample. This series sample was thoroughly mixed in a plastic bucket, a representative sample taken, and the ash content determined. This last was carried out by reducing the representative sample by "coning and quartering" to about 50 gms., grinding in a mortar to pass 100% through a 50 mesh sieve, and doing four ash determinations on this material.

Before any series samples were taken from the bin, however, the ash content of the material at the top surface of the bin was determined to obtain an idea of the figure to be expected.

Average ash content of material at top of bin = 36.6%. Now since Limestone on ignition loses weight in the ratio of 100/56, this figure is not an accurate one for giving the coal content of the material, i.e. the true percentage of coal in the material is not (100 - 36.6)%. It is nearer (100 - 36.6 x 100/56)%.

The Problem of Recovery.

It is customary for the flotation process to be put on a numerical basis in terms of two variables, Grade and Recovery. Grade is simply the percentage of valuable mineral in the finished concentrate, and Recovery the percentage of the valuable mineral recovered.

With the feed mixture here in use the loss in weight of limestone on ashing makes it rather difficult to calculate the recovery of valuable mineral (here coal) in any one flotation test.

$$\text{Recovery} = \frac{\text{Weight Concentrate} \times \%\ \text{Valuable mineral in Conc.}}{\text{Weight Feed} \times \%\ \text{Valuable mineral in Feed.}}$$

With coal the percentage valuable mineral in any sample becomes $(100 - A)\%$ where $A\%$ is the percentage ash in the sample. Thus if we let,

C = Weight of Concentrate.

F = Weight of Feed

A_1 = Per cent ash in Feed.

A_2 = Per cent ash in Concentrate.

$$\text{Recovery} = \frac{C \times (100 - A_2)}{F \times (100 - A_1)} \times 100\%$$

Since this formula does not take into account the loss in weight of the Limestone on ignition, it may conveniently be known as "Uncorrected Recovery". This figure, although giving an approximate estimate of the recovery, is not very suitable for a theoretical study. One may come nearer the truth, if, ignoring the original ash content (8.36%) of the coal, one assumes that the ash is all Lime (CaO). Thus we obtain a

$$\text{Corrected Recovery} = \frac{C \times (100 - A_2 \times 100/56) \times 100\%}{F \times (100 - A_1 \times 100/56)}$$

$$\text{i.e. Corrected Recovery} = \frac{C \times (56 - A_2)}{F \times (56 - A_1)} \times 100\%$$

It is now proposed to verify that this last recovery figure gives a true value of recovery of the valuable component.

A formula will be first obtained from which can be calculated the organic carbonaceous content of the coal in the mixture. As shown above one cannot deduce the percentage of carbonaceous material in a sample from a simple ash calculation. The true carbonaceous content of the mixture may, however, be obtained as follows.

In the Coal/Calcium Carbonate mixture under consideration, let

"(c)"	represent the proportion of organic carbonaceous matter.
"(A)"	represent the proportion of non-calcareous ash. (i.e. the ash content of the original coal).
"(CaO)"	represent the proportion of Lime ash present.
"(CO_2)"	represent the proportion of Carbon Dioxide evolved in ashing process.
"($CaCO_3$)"	represent the proportion of Calcium Carbonate in the mixture before ashing.

In the following analysis it is assumed,

1. that the original ash of the coal contains no lime.
2. that under the conditions of the standard ashing test the reaction $CaCO_3 \rightarrow CaO + CO_2$ goes to completion.
3. that the Limestone is 100% $CaCO_3$.
4. that in the ash of the concentrates the ratio $\frac{(A)}{(CaO)}$ is constant.

This last assumes that the original ash of the coal and the Calcium Carbonate are equally non-floatable. This is the least likely of the four assumptions, but it does not materially affect the result due to the low value of the original ash content.

Then if u = % ash in mixture, i.e. (A) + (CaO)

100 - u = volatile material in mixture, i.e. (c) + (CO_2)

and if v = % ash in original coal

100 - v = % Carbonaceous matter in original coal.

Thus we have the relationships

$$\frac{(A)}{(c)} = \frac{v}{100 - v} \tag{34}$$

$$\frac{(A)}{(c) + (A)} = \frac{v}{100} \tag{35}$$

$$\frac{(c)}{(c) + (A)} = \frac{100 - v}{100} \tag{36}$$

$$\frac{(A) + (CaO)}{(c) + (CO_2)} = \frac{u}{100 - u} \tag{37}$$

$$\frac{(A) + (CaO)}{(c) + (A) + (CaO) + (CO_2)} = \frac{u}{100} \tag{38}$$

We have also the stoichiometric relationships

$$\frac{CaO}{CaCO_3} = \frac{56}{100} \tag{39}$$

$$\frac{CO_2}{CaCO_3} = \frac{44}{100} \tag{40}$$

Substituting for (A), (CaO) and (CO_2) in equation No. 37 we get,

$$\frac{\frac{v(c)}{100-v} + \frac{56}{100}(CaCO_3)}{(c) + \frac{44}{100}(CaCO_3)} = \frac{u}{100-u}$$

i.e. $\frac{(c)v(100-u)}{(100-v)} + \frac{56}{100}(100-u)(CaCO_3) = u(c) + \frac{44u}{100}(CaCO_3)$

i.e. $(c)\left\{u - \frac{v(100-u)}{(100-v)}\right\} = \frac{(CaCO_3)}{100}\left\{56(100-u) - 44u\right\}$

i.e. $100\frac{(c)(u-v)}{(100-v)} = (CaCO_3)(56-u)$

thus $$\frac{(c)}{(CaCO_3)} = \frac{(56-u)(100-v)}{100(u-v)} \tag{41}$$

From this ratio the percentage of carbonaceous material is given by

$$\% (c) = \frac{(c)}{(CaCO_3) + (c) + (A)} \quad x\ 100$$

Thus combining equations No. 36 and No. 41

$$\% (c) = \frac{(56-u)(100-v)}{100(u-v)-(56-u)(100-v) \ x \ \frac{100}{(100-v)}} \quad x\ 100$$

$$\text{i.e. } \% (c) = \frac{(56-u)(100-v)}{(56-v)}$$

Now for the coal being used, v = 8.36%

$$\therefore \%(c) = (56-u)\ \frac{91.64}{47.64} = 1.923(56-u)$$

e.g. For the mixture at the top of the bin u = 36.6%

$$\therefore \%(c) = 1.923(56 - 36.6)$$

$$= 37.3\%$$

Now true recovery is given by

$$\frac{C \ x \ \%(c)_1}{F \ x \ \%(c)_2} \quad x\ 100\%$$

Where C and F are as before the weights of concentrate and feed; $\%(c)_1$ is the percentage carbonaceous material in the concentrate and $\%(c)_2$ is the percentage carbonaceous material in the feed mixture. When one puts the formula for %(c) into the recovery equation it is seen to reduce to

$$\text{Recovery} = \frac{C \ x \ (56-u_1)}{F \ x \ (56-u_2)} \quad x\ 100\%$$

and since u_1 and u_2 have the same significance as A_1 and A_2 used in the "Corrected Recovery" formula, we see that the "Corrected Recovery" formula gives the true recovery figure.

Experimental.

All the quantitative tests given below were carried out in the Fagergren flotation machine described previously. The feed used was that described above. The water was the normal tap water. In Glasgow this is quite soft and has a low solid content. It is therefore quite interchangeable with distilled water for these tests.

The Reproducibility of the Flotation Test.

This consisted of a series of five similar flotation tests. 600 gms. feed material and 2200 c.cs. water were placed in the cell and the rotor set in motion. Six drops of known weight of Pine Oil A were added and conditioning carried out for two minutes with the air cock closed. The cock was then opened and frothing carried out for two minutes. All the concentrate had passed over in about one and a half minutes. The air cock was again closed and all concentrate that had adhered to the sides of the cell and not passed over the launder was wiped back into the cell by means of a rubber "policeman" on the end of a glass rod. This was carried out during the interval of one minute. The air cock was then opened and frothing carried out for one further minute. It was very rarely that any material came over in this last minute. The pan in which the frothed concentrate was collected had been weighed previously; it was now weighed containing the concentrate. The solid material was carefully filtered off in a Buchner funnel, dried in an air oven and weighed. The dried cake was then powdered in a mortar, a representative sample taken, and an ash determination carried out in duplicate. The weight of Pine Oil used per test was estimated by weighing various numbers of drops of the material from the same dropper as used in the tests. The results obtained are shown in Table XXIX.

Table XXIX

Flotation tests - Series I.

Weight Feed = 600 gms. Per cent ash in feed = 38.3%

Volume of water in cell = 2200 c.cs.

Pine Oil added = 0.0580 gms.
= 0.216 lbs. per ton feed.

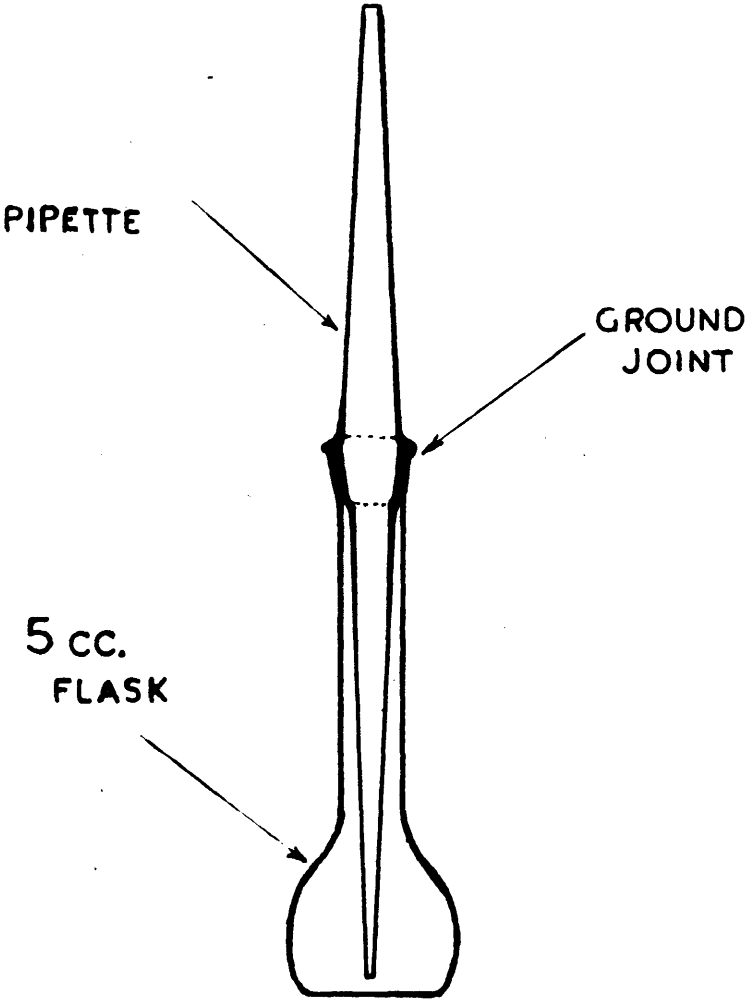
Conc. of Pine Oil = 0.0264 gms./litre.

Test No.	1.	2.	3.	4.	5.
Wt. Pan (gms.)	375.1	404.1	379.1	340.2	341.2
Wt. Pan and frothed Conc.	770.0	847.6	937.9	681.8	601.5
Wt. Frothed Conc.	394.9	443.5	558.8	341.6	260.3
Wt. dried Conc.	54.9	83.5	87.6	63.5	51.6
% Ash in Conc.	12.4	12.8	12.6	14.7	11.6
Volume frothed (c.cs.)	340.0	360.0	471.2	278.1	208.7
Volume frothed/ gm. Pine Oil (c.cs.)	5862	6207	8125	4795	3599
Wt. dried Conc./ gm. Pine Oil (gms.)	946.6	1440	1510	1095	889.6
Conc. Pulp Density (% solids).	13.9	18.8	15.7	18.6	19.8
Recovery					
Uncorrected	13.0	19.7	18.8	14.6	12.3
Corrected	27.8	41.8	44.1	30.2	25.6

It can be seen that there is quite a large variation among the tests; too large for accurate work. This variation is most probably due to a corresponding variation in the amounts of Pine Oil added per test, since it is difficult to make a dropper deliver always exactly the same amount of material. It may also be that an insufficiently long interval was allowed between the time of starting the rotor and the time of adding the Pine Oil. The accuracy of the tests was also affected by the fact that during agitation splashing was apt to occur and material passed down the launder before the Pine Oil was actually added. This last difficulty was overcome by constructing a gate from ¼" sheet Perspex moulded and shaped to fit neatly into the mouth of the Launder. It was held in place by a rubber band and could be easily removed on the instant that frothing started. In order to know accurately how much Pine Oil had been added, a small dispensing bottle was constructed from a 5 c.cs. graduated flask as shown in Figure 78. In use this bottle and its attached pipette were weighed, some material was sucked up into the pipette, the pipette removed and a number of drops dispensed, and the pipette and bottle again weighed. These together with other refinements in technique were employed in the second series of tests which were carried out as follows.

600 gms. of feed material and 2200 c.cs. water were placed in the cell and the rotor set in motion. Agitation was allowed to go on for exactly five minutes. Six drops of Pine Oil A were added from the dispensing bottle, and the

FIGURE 78



DISPENSING BOTTLE
&
PIPETTE

SCALE ~ FULL SIZE

Wm. Gibb

conditioning carried out for two minutes. The air cock was then opened and frothing allowed to take place for two minutes. The sides of the cell were cleaned and refrothing carried out for one further minute as explained above. The frothed concentrate was then treated as in the first series of tests. The results for this second series are given in the Table XXX. They can be seen to be very much more reproducible than the previous series and well within the limit of the experimental error of the method. This method of testing was therefore strictly adhered to in the following work.

Tests on Pine Oils, etc.

These were carried out with varying amounts of each reagent as described above. Where the froth was very copious an initial frothing time of two minutes was not adhered to but instead frothing was continued till no more came over. In some cases, e.g. at high concentrations of Terpineol this was as much as 15 mins. In some cases the reagents were added dropwise and in others as volumes of a saturated aqueous solution. In the latter case care was taken to ensure that the final initial volume of water in the cell was always 2200 c.cs. The following reagents were tested. Pine Oil G.N.S. No. 5, Pine Oil A, Pine Oil B, each added dropwise; Terpineol, added both dropwise and as a solution in water; Fenchyl Alcohol, Camphor and Borneol, added as solutions in water; and Anethole and Dipentene added dropwise. The experimental results are fully tabulated below and the required graphs drawn. Only corrected recoveries were calculated.

TABLE XXI.

Flotation Tests - Series II. **Pine Oil A.**

Weight of Feed = 600 gms. Per cent Ash in Feed = 37.2%

Volume of water in cell = 2200 c.cs.

Test No.	1.	2.	3.	4.	5.	6.
Wt. Pan (gms.)	375.6	404.1	378,3	340.5	341.1	390.0
Wt. Pine Oil added (gms.)	0.0671	0.0669	0.0672	0.0686	0.0659	0.0671
(lbs./ton Feed)	0.251	0.250	0.251	0.256	0.246	0.251
(gms./ltr. water)	0.0305	0.0304	0.0306	0.0312	0.300	0.0305
Wt. Pan and frothed Conc.	941.7	968.5	940.2	918.1	859.5	955.4
Wt. frothed Conc.	566.1	564.4	561.9	577.6	518.4	565.4
Wt. dried Conc.	100.8	106.8	101.8	101.2	95.8	99.7
% Ash in Conc.	16.6	16.7	14.9	15.5	16.6	16.5
Vol. frothed (c.cs.)	465.3	457.6	460.1	476.4	422.6	465.7
Vol. frothed/ gm.Pine Oil.(c.cs.)	6936	6841	6847	6945	6412	6940
Wt. dried Conc./ gm. Pine Oil (gms.)	1502	1596	1515	1475	1454	1486
Conc. Pulp Density (% solids)	17.8	18.9	18.1	17.5	18.5	17.6
Recovery						
Uncorrected %	22.3	23.6	23.0	22.7	21.2	22.1
Corrected, %	35.2	37.2	37.1	36.5	33.4	34.9

Mean values of above Figures.

Average weight Pine Oil added	0.0671	gms.
Average Wt. dried Conc. (at 0.0671 gms.)	101.0	gms.
Average Vol. frothed (at 0.0671 gms.)	458.9	c.cs.
Average Vol. frothed/gm. Pine Oil	6820	c.cs.
Average Wt. Conc./gm. Pine Oil	1505	gms.
Average Recovery		
Uncorrected	22.5%	
Corrected	35.7%	
Average Pulp Density (% Solids)	18.1	

TABLE XXXI.

Flotation Tests - Series III **Pine Oil G.N.S. No. 5.**

Weight Feed = 600 gms. Per cent Ash in Feed = 37.8

Volume of Water in cell = 2200 c.cs.

Method - Agitated 5 mins.; Added Pine Oil dropwise.; Conditioned 2 mins.; Frothed 2 mins.; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.	6.
Wt. Pine Oil (gms.)	0.0438	0.0662	0.0860	0.1091	0.1451	0.1781
- (lbs/ton feed)	0.156	0.247	0.321	0.407	0.542	0.665
- (gms/litre water)	0.0119	0.0301	0.0391	0.0496	0.0660	0.0810
Wt. Frothed Conc.(gms.)	164.0	545.7	911.5	963.6	1022.2	1045.4
Wt. dried Conc. (gms.)	31.7	101.1	164.8	209.0	222.1	225.0
% Ash in Conc.	10.2	13.5	14.1	14.2	14.3	14.3
Vol. frothed (c.cs.)	132.3	444.6	746.7	754.6	800.1	820.4
Vol. frothed/gm. Pine Oil (c.cs.)	3021	6716	8682	6916	5514	4607
Dry Conc./gm.Pine Oil (gms.)	723.8	1527	1916	1915	1531	1264
Concentrate Pulp Density (% Solids)	19.3	18.5	18.1	21.7	21.7	21.5
Recovery of Coal Corrected, %	13.3	39.4	63.3	80.0	84.8	85.9

TABLE XXXII.

Flotation Tests - Series IV. **Pine Oil A.**

Weight Feed = 600 gms. Per cent Ash in Feed = 37.5

Volume of water in cell = 2200 c.cs.

Method - Agitated 5 mins.; Added Pine Oil Dropwise; Conditioned 2 mins.; Frothed 2 mins.; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.	6.
Wt. Pine Oil (gms.)	0.0440	0.0885	0.1049	0.1275	0.1454	0.1710
- (lbs/ton Feed)	0.164	0.330	0.391	0.476	0.543	0.638
- (gms/litre water)	0.0200	0.0402	0.0477	0.0580	0.0661	0.0778
Wt. Frothed Conc.(gms.)	162.3	848.9	970.4	1048.2	1052.8	1091.4
Wt. dried Conc. (gms.)	31.3	156.4	197.4	217.7	201.6	253.1
% Ash in Conc.	11.5	15.3	14.7	14.4	14.6	14.7
Vol. frothed (c.cs.)	131.0	692.5	773.0	830.5	851.2	838.3
Vol. frothed/gm. Pine Oil (c.cs.)	2977	7825	7369	6515	5853	4903
Dry Conc./gm. Pine Oil (gms.)	711.2	1716	1881	1708	1387	1480
Concentrate Pulp Density (% Solids)	19.3	18.4	20.4	20.8	19.1	23.2
Recovery of Coal Corrected, %	12.6	57.4	73.5	81.6	75.2	94.2

XXXIII.
TABLE

Flotation Tests - Series V. **Pine Oil B.**

Weight Feed = 600 gms. Per cent Ash in Feed = 37.2

Volume of water in cell = 2200 c.cs.

Method - Agitated 5 mins.; Added Pine Oil dropwise; Conditioned 2 mins.; Frothed 2 mins.; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.	6.
Wt. Pine Oil (gms.)	0.1098	0.1354	0.1661	0.2009	0.2322	0.2656
- (lbs/ton Feed)	4.09	5.06	6.19	7.49	8.67	9.90
- (gms/litre water)	0.0498	0.0616	0.0755	0.0913	0.1056	0.1207
Wt. Frothed Conc.(gms)	153.4	351.3	571.4	882.5	919.9	1132.6
Wt. Dried Conc. (gms.)	33.6	70.0	100.7	156.5	171.6	226.9
% Ash in Conc.	11.5	12.7	15.0	16.7	16.4	20.6
Vol. water frothed(c.cs)	119.8	281.3	470.7	626.0	748.5	905.7
Vol. frothed/gm. Pine Oil (c.cs.)	1091	2078	2833	3117	3222	3410
Dry Conc./gm. Pine Oil (gms.)	306.0	517.1	606.1	779.1	738.9	854.3
Concentrate Pulp Density (% Solids)	21.9	19.9	17.6	17.7	18.7	20.0
Recovery of Coal Corrected, %	13.23	26.8	36.6	54.5	60.1	71.2

TABLE XXXIV.

Flotation Tests - Series VI **Terpineol (1)**

Weight Feed = 600 gms. Per cent Ash in Feed = 37.7

Volume of water in cell = 2200 c.cs.

Method - Agitated 5mins.; Added Terpineol dropwise; Conditioned 2 mins.; Frothed till no more froth passed over; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.	6.
Wt. Terpineol (gms.)	0.0467	0.0740	0.0782	0.1353	0.1573	0.1709
- (lbs/ton Feed)	0.174	0.376	0.292	0.305	0.587	0.637
- (gms/litre water)	0.0212	0.0336	0.0355	0.0616	0.0715	0.0777
Wt. Frothed Conc.(gms)	333.7	835.1	1031.0	1103.0	1216.8	1241.7
Wt. dried Conc.(gms.)	56.4	157.4	220.9	269.0	286.2	240.2
% Ash in Conc.	10.8	11.1	11.8	12.2	12.4	14.8
Vol. Water Frothed (c.cs.)	277.3	677.7	801.1	834.0	930.6	1001.5
Vol. Froth/gm.(c.cs.)	5939	9160	10360	6165	5917	5861
Dry Conc./gm(gms.)	1208	2127	2824	1988	1820	1406
Conc.Pulp Density (% Solids)	16.9	18.9	21.3	24.4	23.5	19.4
Recovery of Coal Corrected, %	23.2	64.3	88.9	107.1	113.6	90.2

TABLE XXXV.

Flotation tests - Series VII **Terpineol (2)**

Weight Feed = 600 gms. Per cent ash in feed = 36.0

Volume of water in cell = 2200 c.cs.

Method - Agitated 5 mins.; Added volume of saturated Terpineol solution in water and further water to make total water volume 2200 c.cs.; Conditioned 2 mins.; Frothed till no more passed over; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.	6.	7.	8.
Wt. Terpineol (gms.)	0.0198	0.0396	0.0594	0.0990	0.1980	0.2970	0.3960	0.9900
- (lbs./ton feed)	0.074	0.148	0.222	0.369	0.738	1.107	1.476	3.690
- (gms./litre water)	0.009	0.018	0.027	0.045	0.090	0.135	0.180	0.450
Wt. frothed Conc. (gms.)	48.8	460.7	808.9	1060.1	1003.6	1060.1	1067.7	1094.1
Wt. Dried Conc. (gms.)	8.5	72.4	144.8	228.1	207.3	221.1	221.8	219.5
% Ash in Conc.	15.6	12.0	10.5	10.6	10.8	11.5	11.5	11.8
Vol. water frothed(c.cs.)	40.3	388.3	664.1	832.0	796.3	839.0	845.9	874.6
Vol. frothed/gm.(c.cs.)	2035	9804	11180	8405	4022	2825	2156	883.5
Wt. Dry Conc./gm.(gms.)	429.2	1828	2437	2304	1047	744.4	560.1	221.7
Conc. Pulp Density (% Solids)	17.4	15.7	17.9	21.5	20.7	20.9	20.8	20.1
Recovery of Coal Corrected, %	2.86	26.5	54.9	86.4	78.1	82.0	82.2	80.8

TABLE XXXVI.

Flotation Tests - Series VIII **Borneol.**

Weight Feed = 600 gms. Per cent Ash in Feed = 34.8

Volume of water in cell = 2200 c.cs.

Method - Agitated 5 mins.; Added volume of saturated Borneol solution in water and further water to make total volume 2200 c.cs.; Conditioned 2mins.; Frothed till no more froth passed over; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.	6.	7.
Wt. Borneol (gms.)	0.02091	0.03485	0.04879	0.0697	0.1394	0.2091	0.2788
- (lbs./ton Feed)	0.078	0.130	0.182	0.260	0.520	0.780	1.040
- (gms./litre water)	0.0095	0.0159	0.0222	0.0317	0.0634	0.0950	0.1268
Wt. Frothed Conc. (gms.)	142.9	482.2	738.4	846.8	1046.5	961.5	992.9
Wt. dried Conc. (gms.)	27.7	92.3	147.4	185.8	196.2	190.2	198.2
% Ash in Conc.	11.9	11.7	13.3	14.4	13.3	13.9	13.1
Vol. water frothed (c.cs.)	115.2	389.9	591.0	661.0	850.3	771.3	794.7
Vol. frothed/gm. (c.cs.)	5511	10930	12120	5984	6099	3690	2850
Wt. Dry Conc./gm.(gms.)	1325	2588	3021	2667	1407	909.7	710.9
Conc. Pulp Density (% solids)	19.4	19.1	20.0	22.0	18.8	19.8	20.0
Recovery of Coal Corrected, %	11.1	37.1	57.1	70.1	76.0	72.7	77.2

TABLE XXXVII.

Flotation Tests - Series IX. **Fenchyl Alcohol.**

Weight feed = 600 gms. Per cent Ash in Feed = 35.5

Volume of water in cell = 2200 c.cs.

Method - Agitated 5 mins.; Added volume of saturated Fenchyl Alcohol solution in water and further water to make total volume of water 2200 c.cs.; Conditioned 2 mins.; Frothed till no more froth passed over; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.	6.
Wt. Alcohol (gms.)	0.039	0.065	0.091	0.130	0.260	0.390
- (lbs/ton feed)	0.146	0.243	0.340	0.486	0.971	1.456
- (gms./litre water)	0.0177	0.0296	0.0414	0.0592	0.1182	0.1774
Wt. of frothed Conc. (gms.)	144.2	415.9	468.6	553.6	562.9	628.8
Wt. dried Conc. (gms.)	31.8	97.4	118.1	130.4	151.1	162.4
% Ash in Conc.	10.4	9.0	8.9	8.9	9.2	10.10
Vol. water frothed (c.cs.)	112.4	318.5	350.5	423.2	411.8	466.4
Vol. frothed/gm. (c.cs.)	2885	4910	3850	3255	1584	1196
Wt. dry Conc./gm. (gms.)	816	1498	1299	1003	582	417
Conc. Pulp Density (% Solids)	22.1	23.4	25.2	23.6	26.9	25.8
Recovery of Coal Corrected %	11.8	37.2	45.3	50.0	57.6	60.7

TABLE XXXVIII.

Flotation Tests - Series X **Camphor.**

Weight Feed = 600 gms. Per cent Ash in Feed = 37.2

Volume of water in cell = 2200 c.cs.

Method - Agitated 5 mins.; Added volume of saturated Camphor solution in water and further water to make total volume of water 2200 c.cs.; Conditioned 2 mins.; Frothed till no more froth passed over; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.	6.	7.	8.
Wt. Camphor (gms.)	0.0340	0.0510	0.0850	0.1050	0.1700	0.3400	0.5100	0.6800
- (lbs/ton feed)	0.127	0.190	0.317	0.392	0.635	1.270	1.903	2.540
- (gms./litre water)	0.0155	0.0232	0.0386	0.0477	0.0773	0.1550	0.2320	0.3090
Wt. of frothed Conc. (gms)	175.0	415.0	705.5	850.1	904.8	976.9	1066.5	1103.3
Wt. dried Conc. (gms.)	37.2	89.4	151.7	171.7	185.3	203.9	231.3	239.0
% Ash in Conc.	9.7	11.6	12.1	12.8	12.3	12.5	12.6	12.6
Vol. water frothed (c.cs.)	137.8	325.6	553.8	678.4	719.5	773.0	835.2	964.3
Vol. frothed/gm. (c.cs.)	4053	6384	6667	6462	4233	2274	1632	1272
Wt. dry Conc./gm. (gms.)	1094	1753	1784	1635	1090	599.6	453.5	351.5
Conc. Pulp Density (% Solids)	21.3	21.5	21.5	20.2	20.5	20.9	21.7	21.6
Recovery of Coal Corrected, %	15.3	35.2	59.0	65.7	71.8	78.5	88.8	91.8

TABLE XXXXI.

Flotation Tests - Series XI **Anethole**

Weight Feed = 600 gms. Per cent Ash in Feed = 34.8

Volume of water in cell = 2200 c.cs.

Method - Agitated 5 mins.; Added Anethole dropwise; Conditioned 2 mins.; Frothed 2 mins.; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.	6.
Wt. Anethole (gms.)	0.2617	0.3084	0.3193	0.4446	0.5388	0.6407
- (lbs/ton Feed)	0.976	1.151	1.131	1.651	2.010	2.392
- (gms/litre water)	0.1199	0.1403	0.1451	0.2023	0.2450	0.2912
Wt. frothed Conc. (gms.)	52.2	80.4	136.6	920.9	1003.4	1027.7
Wt. dried Conc.(gms.)	9.9	14.9	28.6	186.3	198.1	197.2
% Ash in Conc.	18.0	10.6	11.5	14.7	17.2	15.9
Vol. water frothed (c.cs.)	42.3	65.5	108.0	732.5	905.3	830.5
Vol. frothed/gm.(c.cs.)	161.6	212.3	338.3	1652	1680	1296
Wt. dry Conc./gm(gms.)	37.8	48.3	89.6	419.0	367.7	207.6
Conc. Pulp Density (% Solids)	19.0	16.5	20.9	20.2	18.7	19.2
Recovery of Coal Corrected, %	3.50	6.14	11.54	69.9	69.7	71.8

TABLE XXXX.

Flotation Tests - Series XII **Dipentene**

Weight Feed = 600 gms. Per cent ash in feed = 34.3

Volume of water in cell = 2200 c.cs.

Method - Agitated 5 mins.; Added Dipentene dropwise; Conditioned 2 mins.1 Frothed 2 mins.; Reconditioned 1 min.; Refrothed 1 min.

Test No.	1.	2.	3.	4.	5.
Wt. Dipentene (gms.)	0.3410	0.4728	0.4954	0.7687	0.9283
- (lbs./ton Feed)	1.272	1.763	1.850	2.870	3.470
- (gms/litre water)	0.155	0.214	0.225	0.350	0.422
Wt. frothed Conc. (gms.)	83.0	195.2	303.0	956.0	1097.8
Wt. dried Conc. (gms.)	18.6	45.2	66.0	198.4	243.1
% Ash in Conc.	14.0	15.5	15.1	17.9	18.4
Vol. water frothed (c.cs.)	64.4	150.0	237.0	757.6	854.7
Vol. frothed/gm. (c.cs.)	188.8	317.8	478.3	985.4	921.0
Wt. Dry Conc./gm. (gms.)	54.5	132.5	133.2	258.1	261.9
Conc. Pulp Density (% Solids)	22.4	23.2	21.8	20.8	22.1
Recovery of Coal Corrected, %	6.00	14.42	21.0	58.1	70.2

Discussion of Results.

The results obtained are plotted in Figures 79-82. An attempt has been made to include all the reagents tested in one sheet, but since such a large concentration range had to be covered, the curves tend to be clustered together at one side and spread out at the other. Each graph might be put on a separate sheet to avoid any confusion but in that case one might miss valuable comparisons. All the graphs have been plotted to a base of concentration of reagent in gms. per litre. This was thought to be a more useful variable than lbs. per ton feed mixture, although any value on the one system can easily be converted to the other by the simple use of a factor.

The curves for the reagents can be divided into two groups:-

(a) The frothers; i.e. the Pine Oils, Terpineol, Fenchyl Alcohol, Borneol, and Camphor,

(b) The stabilizers; i.e. Anethole, and Dipentene.

Since these two groups are separated by a relatively large concentration interval, it was decided not to plot the figures for the stabilizers except on one sheet, viz., the recovery curve on Figure 81. In this way the figures have been kept within the bounds of a quarto sheet, while using a fairly large scale on the base line. Thus Figure 82 is merely a repitition of Figure 81 on a larger scale and with the values for Anethole and Dipentene omitted.

Figure 79 indicates the volume of water frothed and this gives a measure of the froth stability of the solution under the conditions of the test, and since the curves cross and re-cross each other in a most bewildering manner, comparison is difficult. In the tables "volume of water frothed per gm. added reagent" has also been evaluated and this gives a better indication of the efficiency of a reagent in forming a froth. Curves connecting volume of water frothed/gm. and concentration of reagent in gms./litre water have not been drawn but it can be seen from the figures that they all pass through a maximum. One might take the value of this maximum for each reagent as a basis for comparison. Thus a study of the tables shows that the reagents appear in descending order of <u>Frothing Efficiency</u> as follows:-

Borneol; Terpineol; Pine Oil G.N.S. No. 5, Pine Oil A, Camphor, Fenchyl Alcohol, Pine Oil B, Anethole, Dipentene.

The Pulp Density of the wet Concentrate can be used as a measure of the solid carrying power of the froth. A study of the pulp densities shows that they are fairly constant for all the reagents; thus it must be concluded that all the reagents tested have a similar carrying power when they form a froth. If the weight of dry concentrate/gm. of reagent is plotted against concentration of reagent in gms./litre one again obtains a curve passing through a maximum. From the tables it can be seen that the maxima are in descending order as above. Thus the amount of solid passed over per gm. added

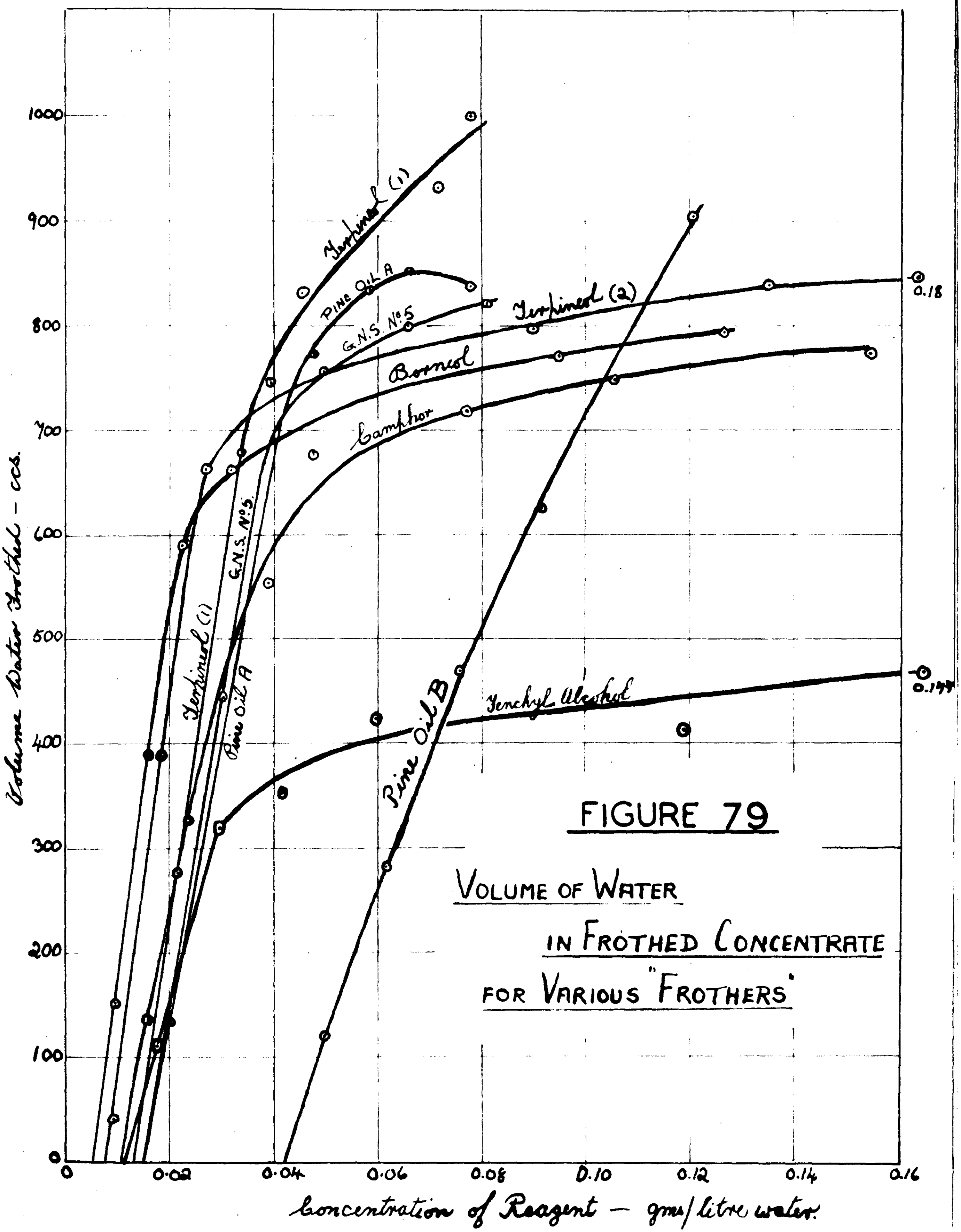


FIGURE 79

VOLUME OF WATER IN FROTHED CONCENTRATE FOR VARIOUS "FROTHERS"

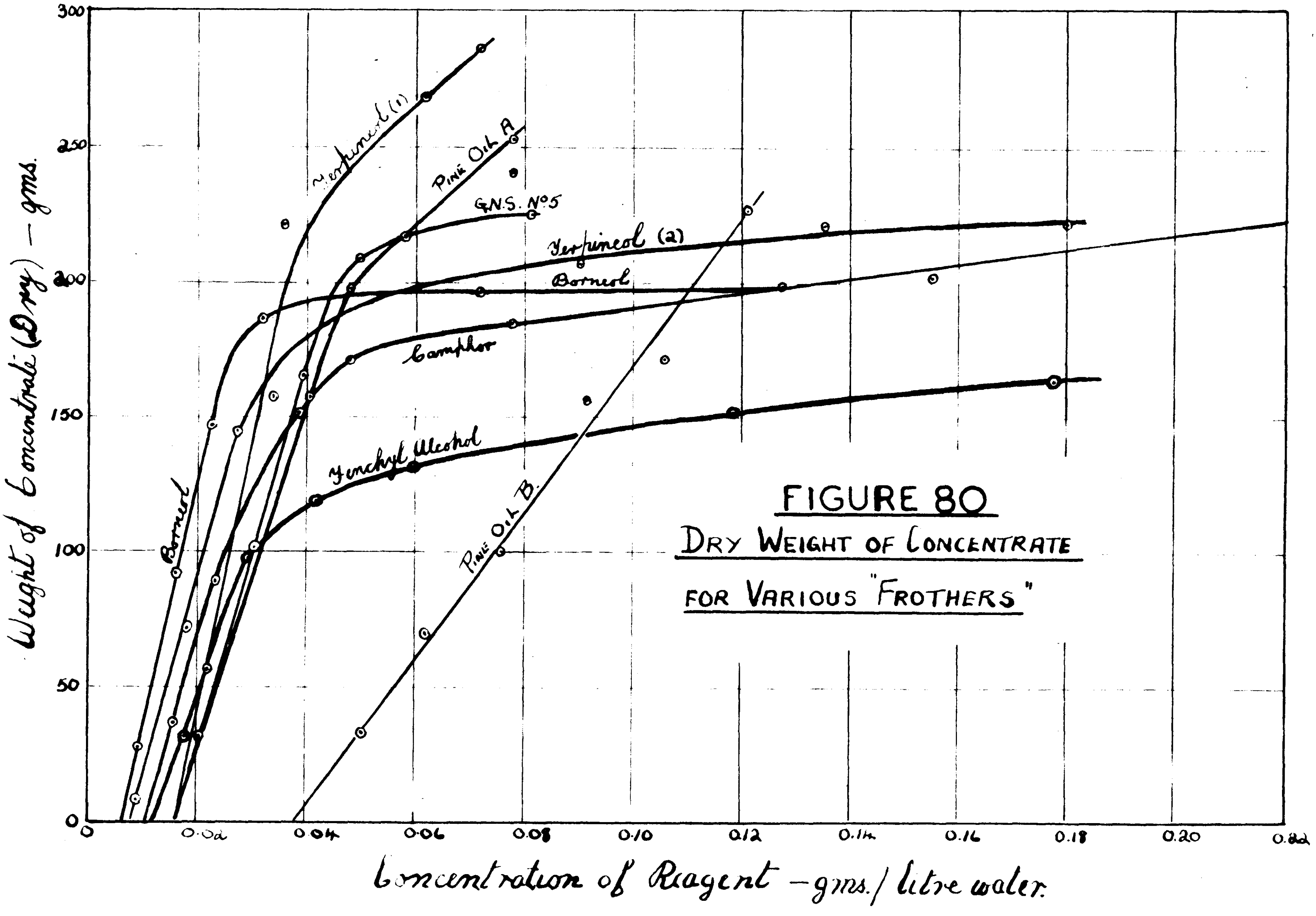


FIGURE 80

DRY WEIGHT OF CONCENTRATE FOR VARIOUS "FROTHERS" reagent again gives a measure of the frothing efficiency of the reagent under test.

Grade.

In the case of coal the ash content may be taken as a measure of the grade of the sample. An attempt was made to plot on one sheet the ash content of all the concentrates against concentration of reagent, but the confusion resulting made comparisons impossible. In some cases at very low concentrations of reagent the small amount of concentrate was found to contain a fairly large proportion of ash, e.g. see Tables XXXV and XXXIX. Since this is contrary to theory, it must be assumed that these results were due more to splashing over the lip of the cell than to true froth formation. A comparison between the reagents was finally achieved in the following way. The reagents were arranged in descending order of grade at minimum ash content, this generally occurring at the lowest concentration of reagent. This was repeated at the maximum ash content of each series. The results are shown in Table XXXXI below.

Table XXXXI.

Reagent	Grade (Per cent Ash)		Order of Merit	
	Maximum	Minimum	At Max. Grade	At Min. Grade
Fenchyl Alcohol	8.9	10.1	1	1
Camphor	9.7	12.8	2	3
Pine Oil G.N.S. No. 5.	10.2	14.3	3	4
Terpineol (2)	10.5	11.8	4	2
Terpineol (1)	10.8	14.8	5	7
Pine Oil A	11.5	14.7	6	6
Pine Oil B	11.5	20.6	6	10
Anethole	11.5	17.2	6	8
Borneol	11.7	14.4	7	5
Dipentene	14.0	18.4	8	9

If one now adds the two merit figures for each reagent and divides each sum by two, one obtains an average merit figure for the concentration range tested for each reagent from which an average order of merit can be derived.

Table XXXXII.

Reagent	Average Order of Merit	
	Merit Figure	Order
Fenchyl Alcohol	1.0	1
Camphor	2.5	2
Terpineol (2)	3.0	3
Pine Oil G.N.S. No. 5.	3.5	4
Terpineol (1)	6.0	5
Pine Oil A	6.0	5
Borneol	6.0	5
Anethole	7.0	6
Pine Oil B	8.0	7
Dipentene	8.5	8

Thus it can be seen that Terpineol added as a solution to the cell is more efficient in floating coal than when added dropwise. This is probably due to the better dispersion achieved.

Recovery of Coal.

One cannot compare the recoveries of coal produced by the various reagents in the same way as above, since a much greater range of values is covered. A qualitative indication is obtained by a study of Figures 81 and 82; curves furthest to the left and furthest up the diagram show the reagents having the largest recoveries for the lowest concentration. Thus the poorest recovery is given by Dipentene, and Anethole is little better. Pine Oil B occupies an intermediate position between these materials and the actual frothers. The frothers can best be seen in Figure 23 which is drawn to a larger scale. For recoveries below 50% the frothers used in solution give better results than those added dropwise. Thus in this range Borneol is most efficient, followed by Terpineol, Camphor and Fenchyl Alcohol. The frothers added dropwise are less efficient and fall off in the order:- Terpineol, Pine Oil G.N.S. No. 5, Pine Oil A, and finally Pine Oil B, with a very low efficiency indeed. At recoveries above 50% there is a complete change over, and the frothers added dropwise become more efficient than the dissolved materials; on the other hand it is difficult to obtain a recovery of more than 80% with a dissolved frother even at high concentrations, since the curves flatten out after a certain concentration is reached. Thus it appears that although the amount of dissolved frother may be increased in an attempt to increase the stability of the froth, there is no corresponding increase in the recovery of Coal. This non-increase in recovery is <u>not</u> due to the increasing flotation

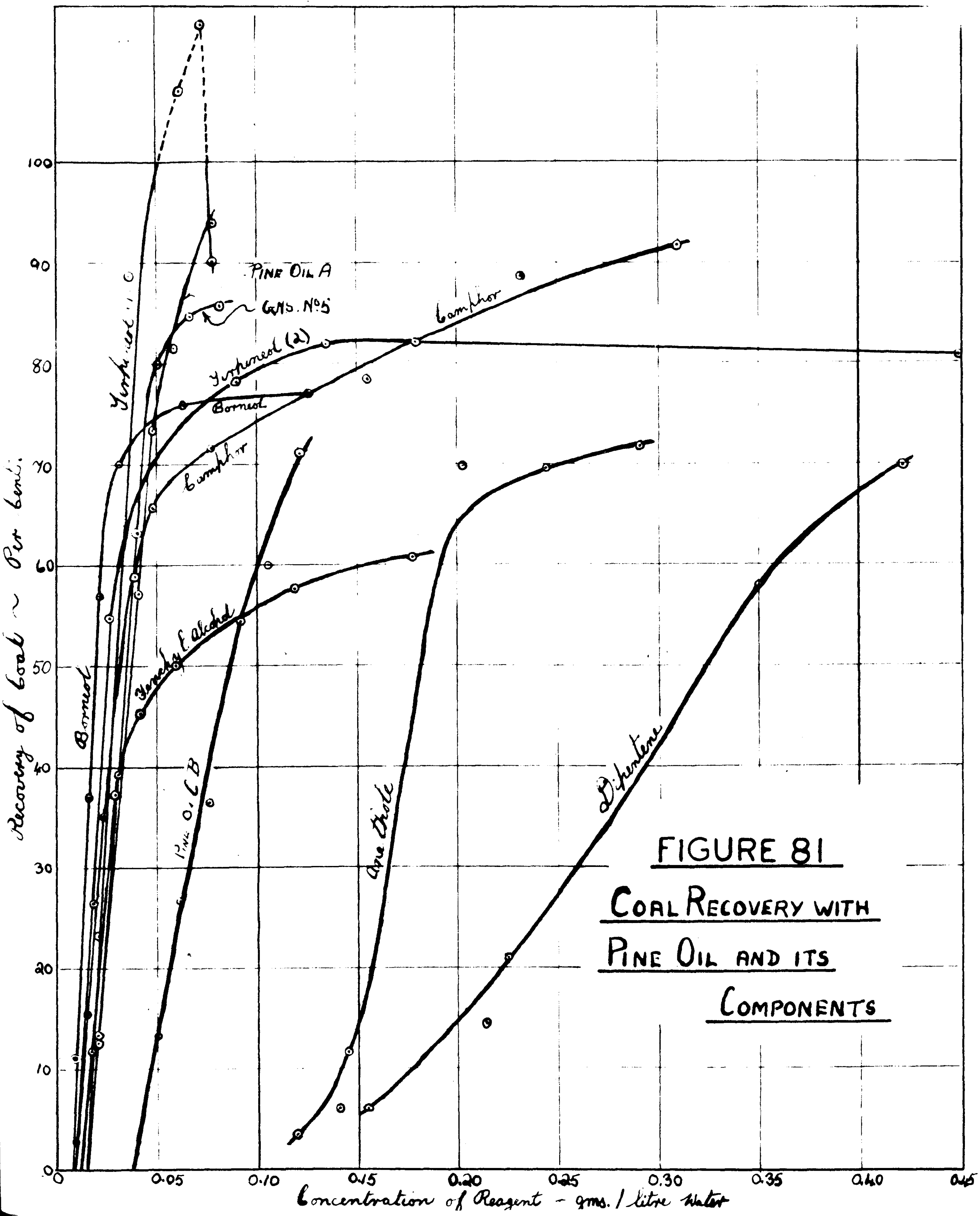


FIGURE 81

COAL RECOVERY WITH PINE OIL AND ITS COMPONENTS

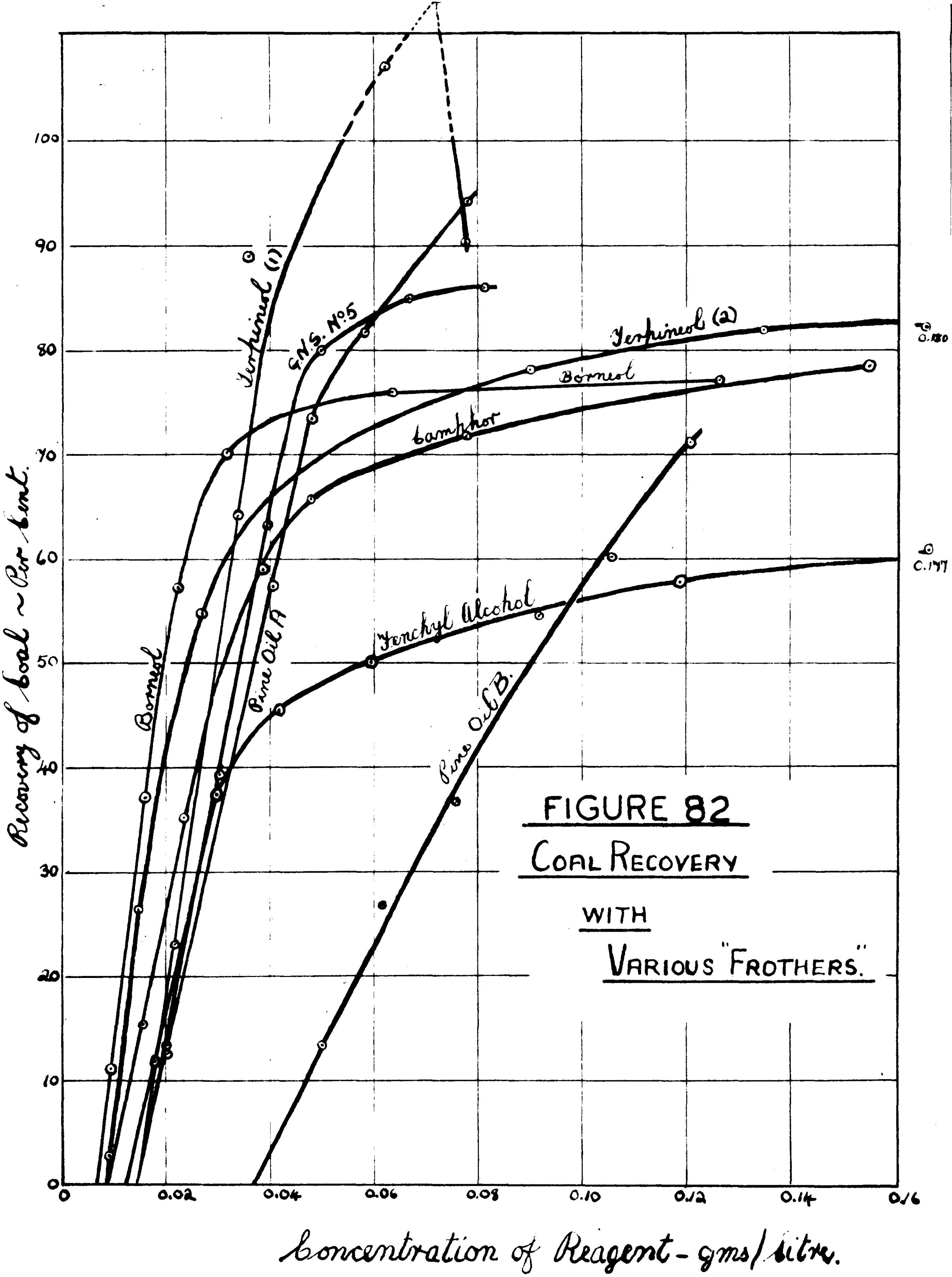


FIGURE 82
COAL RECOVERY
WITH
VARIOUS "FROTHERS".

of Limestone (since the ash content does not increase markedly), but to the non-flotation of the remaining 20% of the coal. It could be assumed that in the two minutes allowed in the flotation tests for dispersion of the reagent added dropwise, solution is not complete and the undissolved material present enhances the stability of the froth. A more attractive solution, however, to the problem is that the undissolved material is used to film the coal to enhance its floatability. It is therefore suggested that the flotation agents used here are not merely creating a froth to which the air avid surfaces of the coal cling, but are also adsorbed on the coal surfaces both in the dissolved and undissolved state.

It has long been supposed that such materials as coal, graphite, etc. are inherently floatable, i.e. they require no collector to give them the necessary non-polar hydrocarbon surface which causes a mineral to adhere to a bubble of air. The Australian school under Wark (2) and the Americans under Taggart (73) have investigated this problem by means of contact angle measurements, but there is no certainty as to whether coal possesses this property or not. The results are made difficult to obtain by the fact that it is extremely difficult to prepare a completely clean coal surface.

In laying down the properties of an ideal frother for flotation work, Dean and Hersberger (74) stipulate, "It must be absolutely noncollecting to both sulphides and non-sulphides."

Now a flotation reagent can only have collecting properties if it is adsorbed on the mineral to be collected.

Terpineol has always been claimed to be a practically ideal frother because it did not collect the common minerals. Figure 82 of this work, however, seems to indicate that adsorption of Terpineol and the other reagents is taking place on the coal for,

(a) the recovery curves do not cut the concentration axis at zero concentration of flotation reagent, i.e., it requires a definite amount of reagent to be in the cell before enough frothing takes place to pass material over the lip of the cell. It is suggested that this minimum quantity (0.007-0.009 gms./litre - in the case of the dissolved materials, Borneol, Fenchyl Alcohol, Camphor and Terpineol) is adsorbed on the coal making it air avid.

(b) the reagents added dropwise, Terpineol, Pine Oil G.N.S. No.5, and Pine Oil A cut this axis at a slightly higher concentration value (0.014-0.015 gms./litre). Since the Pine Oils are mostly composed of Terpineol, one can only assume that the greater concentration is used as undissolved oil which is directly filmed on the coal surfaces. An explanation of the enhanced recovery obtained by the dropwise added reagents is thus available, viz., that the remaining 20% of the coal (probably the larger particles) can only be floated if there is direct filming of the surfaces with undissolved oil. This would increase the contact angle and make it easier for the heavier particles to adhere to the bubbles. Anethole and Dipentene possessing little or no polar properties require about ten times the amount of material before flotation starts, e.g. these materials cut the axis at about 0.13 gms./litre. According to Taggart et al. (75) the filming of coal with a non-polar hydrocarbon is bound up with considerations of mutual solubility of the materials. If there is no mutual solubility there is no filming. This might be the mechanism in the case of these materials. Of course, this is just the same as saying that there is a low interfacial tension at the Coil/Oil interface; cf. the spreading of an oil on water. A final suggestion is rather hesitantly made that if one takes the concentration of 0.007 gms./litre as being equivalent to an adsorbed monolayer, the dropwise-added materials at 0.014 gms./litre have a double layer, i.e. a monolayer plus a layer one molecule thick of undissolved oil, and the non-polar substances have a layer about 20 molecules thick.

Froth Stabilities with and without Solids.

The shape of the curves in Figs. 79-82 raises a number of interesting points which may be explained best by considering ideal cases.

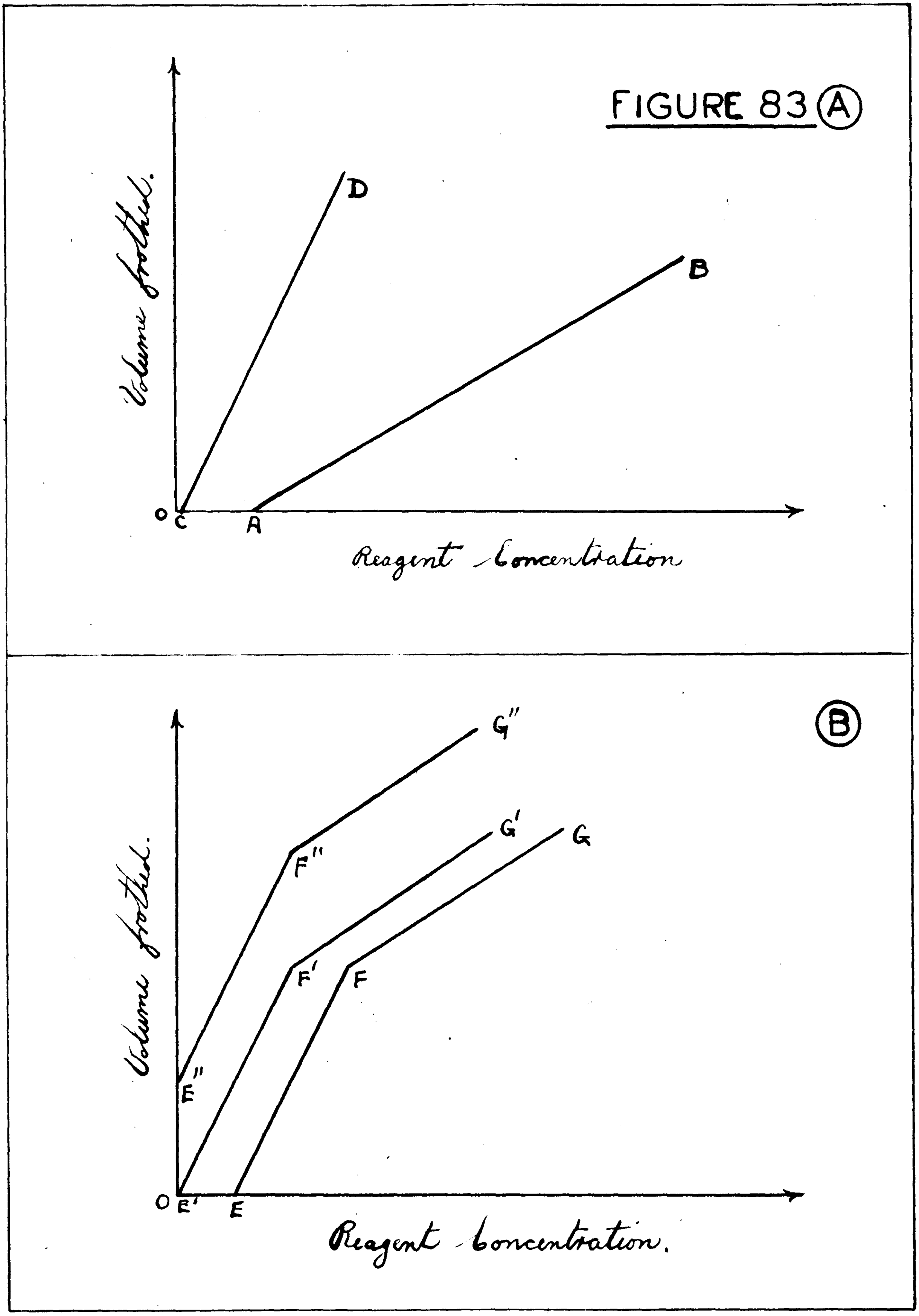
Consider a batch flotation machine of the type used in the above tests and containing water only. If one adds frothing agent to the cell during agitation and aeration, froth begins to pass over and down the launder to the collecting trough as soon as the stability of the froth increases beyond a certain value. The value of this critical stability will depend on the physical dimensions of the cell. i.e. the length of path the froth has to traverse before it is out of the cell. Any froth of a lower stability will remain in the cell. This critical stability will occur at some definite concentration of frothing agent. Due to Gibbs' adsorption of the reagent on the bubble walls the removal of froth from the cell will cause the concentration of frothing agent to drop. Increase in stability much above the critical value will only be evident in the time taken to collapse by froth passed into the collecting trough. For any given concentration of reagent greater than that equivalent to the critical stability, and with the machine supplying air at constant rate, bubbles will continue to pass over until the concentration of frother has decreased to that value at which the bubbles are no longer strong enough.

In a batch type of machine like the Fagergren the volume of water in the cell will have been decreased by the frothing process so that the path that the final bubbles have to traverse to reach the collecting trough will now be greater than at first, and thus the critical stability with its associated concentration of reagent will also be greater.

It is evident that for a given size of flotation cell and rate of air supply the volume of froth (i.e. liquid) collected is proportional only to the concentration of frother, and for large volumes of water will be independent of the volume of water in the cell. For the small range of reagent concentration covered the plot of Volume of liquid frothed against reagent concentration can be considered to be a straight line as shown in Figure 83A. The gradient of this line $\frac{\Delta V}{\Delta C}$ will be constant only where the volume of liquid in the cell does not change much during the process. It gives a measure of the <u>Frothing Power</u> of the frothing reagent.

Turning now to froths containing solids in a condition to be collected by the bubbles. It is well known that solid in this condition stabilizes froth. Thus the critical stability will occur at a lower reagent concentration ; this concentration may be so small as to be taken as practically zero, and since the solid mineral plays a part in stabilizing the froth more material will pass over than previously (i.e. it will need less reagent to produce the same amount of froth), before the reagent concentration is lowered to the critical stability level. Thus the gradient will be increased as shown in Fig. 83A, where AB is the line for a two phase froth and CD is the line for a three phase (i.e. containing solid) froth. OA and OC are the respective reagent concentrations for critical

FIGURE 83


Ⓐ
Volume frothed.
D
B
O
C
A
Reagent Concentration
Ⓑ
Volume frothed.
G''
F''
G'
G
F'
F
E''
O
E'
E
Reagent concentration.

stability.

If sufficient frothing agent is used all collectable solids will be passed over before the reagent concentration has dropped to the critical stability level. The concentration of reagent remaining at this point will control the subsequent volume of liquid passing over, and thus the gradient of the curve of volume frothed/concentration of reagent will change to that of the two phase froth (As AB in Figure 83A) after all solid is passed over. The complete plot will then take the form shown in EFG in Figure 83B. For concentrations of reagent between F and G, the volume of water up to F comes over with solid and the remaining volume as water alone.

EFG is then the ideal case of the curves for the dissolved frothers shown in Figure 79. For Terpineol (2), Borneol, Fenchyl Alcohol and Camphor for concentrations up to about 0.03-0.04 gms./litre water the gradient of the curves is sharp and obviously influenced by the solid present. At higher concentrations the gradient becomes much less due to the fact that all the solid available is already collected and further reagent only carries over water. Furthermore, the relative positions of the curves for these reagents except in the case of Fenchyl Alcohol are now similar to those given by the frothing tube experiments as shown in Figure 76.

Where the frother is also a collector, i.e. a small initial concentration is adsorbed on the mineral before frothing starts, the distance OE will be increased. Thus if a non-adsorbed frother and solid curve cuts the axis at or near the origin when one plots recovery of valuable mineral against concentration of reagent, the distance OE becomes the concentration initially adsorbed as suggested in the previous section.

In the case of a frother and non-frothing collector acting together, three things may happen with increase in concentration of collector.

(a) the concentration of frother for critical stability is further reduced, i.e. the line EFG will move further to left, e.g. $E'F'G'$. (if the collector has itself frothing properties the line may further move till it cuts the volume frothed axis a definite volume of froth for zero concentration of frother, e.g. to $E''F''G''$.)

(b) the gradient of the line (GD and EF) may further increase due to the fact that more solid is available for flotation, and thus for stabilising the froth.

(c) the upper limit of EF will probably rise due to the greater amount of solid available.

In the practical flotation test all these factors will combine to give the shape of curve shown in Figs. 79-82.

FURTHER WORK.

Although it is hoped that the work described in this thesis is complete in itself, a number of possible avenues of future research have been opened up.

Perhaps the most interesting of these would be:-

(a) A further detailed study of the variation of M, the froth volume stability constant, with concentration of the frothing agent in its aqueous solution. This should make M the ultimate criterion of froth stability for these relatively unstable froths. Since, however, froth heights can be measured more accurately than froth volumes, of major importance would be

(b) A study of the effect of the variables on the intercept constants h_1°, (equation No. 26), and K, (equation No. 31), so that it would be possible to correlate the froth height at any rate of air flow in any apparatus with the froth height in any other apparatus merely from a knowledge of the apparatus dimensions.

(c) A study of the frothing properties of the aliphatic aldehydes to link up the results already given for the alcohols and fatty acids. One might spend a lifetime evaluating the concentration for maximum froth stability of all the remaining surface active agents dissolved in water, but of immediate interest would be the determination of the concentration necessary in the surface film for the maximum froth stability of solutions of a number of aromatic compounds, e.g. the phenols. Further extension of the method will be hindered by the lack of accurate surface tension data for the aqueous solutions involved. This would lead naturally to

(d) A study of another popular froth flotation agent, Cresylic Acid. This could be carried out in an exactly similar manner to that used with Pine Oil.

(e) An analysis of the agitation froth flotation machine on the lines of that of the bubble-column machine carried out here. The analysis of the batch machine could also be extended to the continuous flotation process.

(f) A study of the dynamics of three phase froths in a bubble-column, i.e. froths containing solid particles. This brings one into the realm of the force of adhesion of the mineral particle to an air bubble.

(g) A study of the possible adsorption of the terpene derivatives on coal. This could lead to the measurement of the possible adsorption of frothers in general on mineral surfaces. A method is, therefore, required for the measurement of small concentration changes of the surface active agents involved. A reliable Surface Tension method seems the most likely to give accuract results, e.g. Ferguson's method (76), or the method of Maximum Bubble Pressure. Such a method would require an apparatus capable of measuring surface tension of aqueous solutions under all conditions from almost pure water to the mineral suspensions which constitute flotation pulps. The author is at present developing an apparatus capable of measuring surface tension by either of the above mentioned methods and of giving accurate results under the range of conditions encountered in froth flotation practice.

Froth flotation offers a particularly fruitful field for fundamental research, touching as it does on most aspects of physical, inorganic and organic chemistry. Although originally confined to purely mineral concentration, it is now being employed in the most unlikely fields, e.g. from the separation of ergot from rye (77) to the purification of industrial wastes (78). This extension of its application together with the simplicity of the apparatus involved is causing it to be recognised today as one of the more important unit operations of chemical engineering (79).

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