PHYSICOCHEMICAL STUDIES ON DUSTS.

(i) The Ageing of Siliceous Dusts.

(ii) A Comparison between the Solubility and Sorption Properties of Rutile (TiO_2) and Quartz (SiO_2).

(iii) The Preparation of Synthetic Quartz.

by

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SUMMARY.

1. The history of pneumoconiosis is outlined. The various theories advanced to explain silicosis are stated and their validity discussed. This allows the problems chosen for research to be seen in relation to other problems in this field, and provides a general background to the research.

2. The phenomenon of the "ageing" of siliceous dusts, whereby the rate of solubility of the dusts appears to decrease with storage time, has been investigated. The effect of the preparative processes (acid-extraction, washing, and drying), the humidity and gaseous nature of the storage atmosphere, and the absorption of carbon dioxide by the solvent have been examined. The nature of the surface of the dusts after grinding has also been studied.

As a result of the experiments it was concluded that the decrease in solubility of siliceous dusts on storage is the result of the following factors:-

(a) A gradual change in the nature of the modified surface (produced by grinding) from an amorphous to a more crystalline form, of lower solubility.

(b) The humidity of the storage atmosphere and the adsorption or loss of water by the dusts.

(c) The absorption of carbon dioxide by the solvent. The relative importance of each factor varies, and depends on the physical characteristics, (e.g. particle size, crystallinity) of

the dust involved.

3. The physical properties of silica (SiO_2 - fibrogenic) and rutile (TiO_2 - non-fibrogenic) have been compared. The following results were obtained:-

(a) The solubility of rutile at pH 7.5 (the pH of the lung fluids) is so low as to be outwith the sensitivity of the reagent used (i.e. < 1 part in 10^6). Silica has a readily measurable solubility at this pH.

(b) The existence in rutile dusts of a disturbed surface layer of higher solubility than the core, analogous to the "disturbed layer" of quartz, was not detected.

(c) Rutile and quartz were shown to adsorb the same types of dyestuffs (i.e., basic).

(d) Rutile adsorbs three to four times as much basic dye as does quartz.

These results indicate that simple adsorption of materials from the lung fluids plays at the most a small part in the production of silicosis. They provide further evidence in support of the "solubility theory" of silicosis.

4. A method for the synthesis of small crystals of pure quartz has been developed. The development of this method is described. Its use for the investigation of the effect of trace impurities on the physical and fibrogenic properties of quartz is discussed.

INTRODUCTION.

The work described in this thesis is a contribution to the study of the chemistry of silica in relation to the industrial disease silicosis. In order to select the most promising topics for study, the various aspects of the subject are critically reviewed in this introduction.

In Great Britain in 1952 there were altogether 1,905 deaths from fibrosis of the lung, including 677 cases of non-occupational fibrosis. Of the remainder, 586 were classified as silicosis, 573 as pneumoconiosis of coal miners, 12 as asbestosis, 13 as byssinosis, and 44 cases of pneumoconiosis from other industries (1).

These figures indicate the importance of pneumoconiosis (which is a general term covering all dust diseases of the lungs, fibrous and non-fibrous) in modern industry. The best known and most important of the pneumoconioses is silicosis which, at the International Silicosis Conference in South Africa in 1930, was defined as follows:-

"Silicosis is a pathological condition of the lungs due to the inhalation of silicon dioxide. It can be produced experimentally in animals."

Development and Nature of Silicosis (2).

The lungs, being in free communication with the external air and its impurities, are provided by nature with protective devices to prevent the accumulation of foreign particles.

Inhaled air must first pass through a filter of coarse hair in the nose. Thence it goes through a series of tortuous, moist-walled passages where many of the smaller particles are trapped. The remainder of the upper respiratory tract (the pharynx, the trachea, and the bronchi) is lined by cells covered with minute vibratory hairs, the cilia. Particles lodging on the surface of these hairs tend to be carried back whence they came by the vibrations of the hairs.

Dust particles which pass these defences are ingested by the phagocytes, wandering scavenger cells, which tend to carry the dust to a special drainage system, the lymphatics. The dust is then fixed and immobilised in some part of the lung. This mechanism is protective at first, but overlong exposure to high concentrations of dust leads to a considerable accumulation of dust, and pneumoconiosis begins.

The time of exposure to dust required to produce silicosis varies according to the dust concentration, particle-size distribution, the percentage of free silica in the dust, and biological factors including individual susceptibility and the presence or absence of infection (3). The lungs of many men exposed for years to siliceous dust containing a large amount of free silica showed no evidence of having developed silicotic fibrosis (4,5).

In normal lungs, silicosis is manifested by numerous small, uniformly distributed, discrete fibrous nodules, often causing no symptoms. In infected lungs the fibrosis is massive and is accompanied by compensatory emphysema producing dyspnoea. It specifically predisposes to tuberculosis, of which a large but variable proportion of its victims die.

History of Occurrence of Silicosis.

Silicosis is not a "modern" disease, although its incidence is probably much increased by modern methods.

Pliny (6), writing in the 1st Century A.D., states that "Minium refiners in the factory envelope their faces with loose bladders, which enable them to see without inhaling the fatal dust". This is probably the first published recognition of the harmfulness of exposure to dust.

Wilder and Wilson (7) observed evidence of silicosis with pleural adhesions in pulmonary tissues of the Palaeolithic age, and Jones et al. (8) observed pleural adhesions in Egyptian mummies. Considering that the natural rocks worked, in the latter case at least, were granite and sandstone, one can speculate upon the existence of dust diseases of the lungs in those times.

The miners of Egypt, Greece, and Rome were slaves, criminals, and prisoners of war, and were creatures half-way between man and beast.

If dust disease existed (the mines were very wet, and it may not have) it would probably be a pleasant release from the tortures of their existence.

After the fall of the Roman Empire mining was carried on only intermittently until the 10th Century in Central Europe. The miners of this period were free men and had their own guilds.

These miners of Central Europe suffered from a disease known as "Bergsucht" which, as a clinical entity, was a mixture of silicosis, pulmonary neoplasms, and arsenical and mercurial poisoning. The pathogenesis had its roots in demonology, in alchemy, in "humours", and in one or two sound clinical observations.

"Where water in the shafts is abundant and very cold, it frequently injures the limbs, for cold is harmful to the sinews. To meet this, miners should make themselves sufficiently high boots of raw-hide which protect their legs from cold water; the man who does not follow this advice will suffer much ill-health, especially in old-age. On the other hand some mines are so dry that they are completely devoid of water, and this dryness causes the workmen even greater harm, for the dust which is stirred and beaten up by digging penetrates into the windpipe, and produces difficulty in breathing, and disease which the Greeks call asthma (ἆσυμα). If the dust has corrosive qualities it eats away the lungs and implants consumption in the bodies."

Thus Agricola (9), in his "De Re Metallica" published in 1556, described the hazards of mining in his time. Pansa (10), in 1614, was the first writer to discuss miners' lung diseases in detail, and in 1649, Van Diemerbrock (11) made the first section of a stone-cutter's lung in a case of fatal asthma. This revealed "lung vesicles completely clogged with fine dust" such that he thought that he was cutting some sandy body.

By the end of the 17th Century German mining had declined, but by this time the use of gunpowder for underground blasting had been introduced by Weindl, a Tyrolean, and Hutmann had tried out a crude drilling machine. These innovations probably mark the start of the modern dust problem.

The industrialisation of Britain in the 19th Century saw a great increase in occupational dust disease in Britain. From Scotland, in 1831, Gregory (12) reported "a case of peculiar black infiltration of the whole lungs resembling melanosis". Eventually what commenced as an investigation of this "black spit", a peculiar form of melanosis, ended up as a reasonably accurate pathological and clinical concept of silicosis and coal miners' pneumoconiosis.

Until the mid-point of the 19th Century, serious respiratory disease among all types of miners was high, and their mean duration of life was less than average. Towards the end of the Century, however, a strange phenomenon occurred - the "black spit" gradually disappeared until at the end of the Century it was almost forgotten as a medical entity. This was probably brought about by improved ventilation (the introduction of mechanical ventilation) and sanitary conditions.

This was so marked that Collis (13) stated that "asthma has passed almost unobserved from our midst," and Haldane (14) averred, in effect, that coal miners did not contract pneumoconiosis. Official statistics for the time did not support these statements, however, for miners died in excessive numbers from "bronchitis".

In the first quarter of the 20th Century pits became deeper and seams narrower, and mechanisation was introduced without adequate dust suppression. As a result of this, 22,000 British coal miners had to leave the pits, because of pneumoconiosis, between the years 1931 and 1948. In 1949 and 1950 an additional 10,000 cases were diagnosed, and 4,500 of these had to leave the pits. In 1945, out of a total work-force of 700,000 men, there were 5,706 deaths from occupational chest disease.

Pneumoconiosis is now the most serious industrial disease in the country.

Theories of Silicosis.

The mechanism of the disease silicosis is still very obscure, and many theories have been advanced to explain it. Some of these theories are discussed below.

The Mechanical Theory of Silicosis.

Haldane (15), after a study of the pathogenic effects of dusts used in stone-dusting in the mines, concluded that powdered clay, shale, chalk, and other soft, inert materials are harmless, whereas flue-dust, crushed granite, flint, ganister, and other gritty material are dangerous, giving rise to chronic inflammation of the lung tissues. That is to say, the fibrosis is produced by irritation of the soft tissues of the lungs by the hard, sharp edges of the particles.

It is a fact that foreign bodies in the tissue excite a certain amount of reaction which is followed by the production of fibrous tissue. This type of fibrosis is, however, never comparable to the extensive fibrosis of silicosis.

Conclusive evidence against the mechanical theory of silicosis was provided by the experiments of Gardner (16). He showed that silicon carbide dust, the particles of which are very hard and have edges which are as sharp as those of mineral dusts, did not, on introduction to the lungs of animals, produce the typical fibrous reaction brought about by quartz dusts.

The Chemical and Solubility Theories of Silicosis.

In 1918, Lanza (17) suggested that there was a connection between the chemical composition of the dust and its pathogenicity, since the most dangerous dusts contained the greatest amounts of silica.

In 1922, Gye and Kettle (18) provided further evidence of the importance of the chemical composition of the dust. They showed that the subcutaneous injection of silica into animals produced characteristic lesions. These consisted of a central area of necrosis (dead tissues) surrounded by an area of leucocytes (white blood corpuscles) followed by a further zone of necrosis. The whole lesion was bounded by granulation tissue (i.e. tissue which forms when a wound heals when the edges are not in apposition). These workers also concluded that, since tubercule bacilli multiplied rapidly in the necrotic areas, the action of silica must aid the establishment of this infection.

Gardner's experiments (16), in disproving the mechanical theory, also supported the chemical theory of silicosis.

In 1926, Sayers (19) suggested that those dusts which had the highest free-silica content were the most injurious, and that injury to the lung tissues might be caused by a poisonous action of silica dissolved in the lung fluids. This is, in effect, a statement of the chemical theory of silicosis, that the chemical properties of the dust are important as a causative in the production of silicosis.

The report of Heffernan (20) in 1926 on dust conditions arising in the manufacture of Derbyshire ganister bricks showed that workers exposed to this dust did not develop silicosis. The composition of the dust was <u>ca.</u>84% silica and 16% clay and earth, with some organic matter, i.e. a dust with a high free-silica content which did not cause silicosis. This provided an apparent contradiction to the chemical theory. Heffernan concluded, however, that the minor constituents of the dust were exerting some modifying influence on the usual fibrogenic properties of silica. These findings drew the attention of workers in this field to the importance of the effects of minor constituents occurring in natural dusts.

In further supporting the chemical theory Kettle (21) in 1926 propounded a mechanism for the disease. He suggested that the silica dissolved in the lung fluids forming colloidal silicic acid, which acted as a cell poison and produced necrosis. He also concluded that it was the silica itself, rather than the fibrotic condition of the tissues, which promoted the growth of the tubercule bacillus.

In 1932, Kettle (3) investigated the harmfulness of a number of different dusts. He injected mice and rabbits subcutaneously with saline suspensions of the dusts and examined the tissue reaction produced. He found that all the siliceous dusts tested were active, producing necrosis and exciting a pronounced cellular reaction. All the non-siliceous dusts were inert, and remained quiescent at the site of injection. The most valuable part of this work was probably the discovery that a highly toxic quartz dust could be rendered completely innocuous by coating with a thick layer of ferric oxide. He suggested that the ferric oxide layer prevented the silica from dissolving in the lung fluids, and that this accounted for the harmless quality of the dust.

In 1933, Policard (22) showed that dissolved silica acts as a cell poison.

In 1935, Siegmund (23) and Geise (24) confirmed Kettle's findings that only siliceous dusts produced the nodular fibrotic conditions of silicosis and demonstrated conclusively that some chemical property peculiar to silica was responsible for the initiation and development of the pathological changes associated with the disease.

Policard (22) had shown that silica is a cell poison, and it was suggested that the toxicity of a dust was dependant upon the amount of silica it released into solution in the body fluids. Thus the Solubility Theory of silicosis developed from the general, chemical theory.

King (25) has carried out extensive research on the modern solubility theory, and, in general, his results supported the theory. He showed that quartz and flint, which are among the most toxic of the mineral dusts, dissolve to the extent of 10 mg. silica per 100 ml. of blood plasma; whereas shale-dusts, which have a very low pathogenicity, have a solubility of only 1-2 mg. silica per 100 ml. of blood plasma. Moreover, shale dusts markedly depress the solubility of quartz dusts and almost completely inhibit the pathogenic effects in the lungs of animals. King also showed that mica and shale dusts which have been treated with strong mineral acid become more soluble and more pathogenic.

There are, however, some discrepancies in the theory. While it is true that the more soluble forms of silica are the more toxic, it is not true that the most soluble is the most toxic. Gardner (16) found that extremely soluble "20 Angstrom silica" produced as a condensate in furnaces in which silica sand is melted, is without effect on the lungs and livers of experimental animals (presumably because it is eliminated too promptly from the body). Again, certain sandstones of extremely low silica-solubility are almost as pathogenic as quartz; while olivine is of intermediate solubility, but apparently causes no pulmonary disease in man and no fibrosis in the lungs of animals.

Denny, Robson, and Irwin (26) showed that the development of silicosis in animals exposed for long periods to a quartz-laden atmosphere could be prevented by the addition of small quantities of finely divided metallic aluminium powder to the quartz dust. They also showed that the presence of a small amount of metallic aluminium in a quartz dust almost completely inhibited the solubility of the quartz *in vitro*. They demonstrated that this was due to the adsorption of aluminium hydroxide at the quartz surface. This formed a protective coating which prevented contact of the quartz with the liquid bathing it.

Belt and King (27), administering single doses of the mixed dusts to animals by an intratracheal injection technique, could not substantiate these findings. King suggested, however, that the failure of the aluminium to inhibit the disease in these single dose tests was probably due to elimination of the metal by the body, leaving the quartz dust in the lung to continue its normal fibrogenic course.

This suggestion, that the method of administering the dusts was at fault, was borne out by the work of King, Wright, Ray, and Harrison (28), who showed that the development of silicosis in the lungs of rats exposed to an atmosphere heavily laden with quartz dust could be retarded, or possibly prevented, by the addition of 2% aluminium powder to the dust.

The solubility theory of silicosis may, therefore, be accepted as a good general hypothesis. It is, however, incomplete, and has some discrepancies. King has suggested that these may be due to the difficulty of exactly simulating body-processes *in vitro*. Although one dust may dissolve more rapidly than another in solubility tests, this does not prove that the same will be true *in vivo*. He also suggested that the poisonous materials leached from the silica in the lungs may not be identical with those dissolved and determined *in vitro*. He further suggested that there might exist some form of "nascent" silica in solution which could evoke in the body tissues the characteristic fibrotic reaction of silicosis.

The Sericite Theory.

Jones (29), on examination of the rocks from the underground working places of some miners who had contracted silicosis, found that not all of the rock came into the categories which were legally considered dangerous. He decided to investigate the matter.

He examined the rocks and the mineral residues from 29 silicotic lungs. The bulk of the residues were found to consist of minute fibres of the mineral sericite, a hydrated silicate of aluminium and potassium. This mineral was also found to be abundantly present in all the rocks and minerals giving rise to dust which when inhaled has been incriminated as the cause of silicosis. Jones then suggested that these results showed that silicosis is not due to free silica, but to silicate minerals occurring in the form of minute fibres loosely held together in the rocks so that, during handling, drilling, and blasting, they are readily freed into the atmosphere and inhaled into the lungs. He made no suggestion as to how the sericite caused the fibrosis.

This theory aroused considerable discussion. It received much support since it seemed to clarify certain anomalies in relation to dust composition and pathogenicity (30). Many cases of silicosis have been diagnosed among miners at Broken Hill, New South Wales, Australia. The amount of free silica in the ore varies from 1.62 to 17.73%. At Broken Hill, however, there occurs a rock known as "sillimanite-gneiss" in which the aluminium silicate mineral, sillimanite, occurs, generally as minute fibres. Sericite is also abundantly present in some of the rocks. The rocks are, therefore, of low free-silica content, but produce dangerous dust which can be explained on the basis of the sericite theory.

There was also, however, much criticism. Haldane (31) strongly disagreed with Jones' conclusions. He stated that what seemed of importance was not the nature of the dust found in the lungs at the time of death, but the history of prolonged exposure to dust of high free-silica content. He found nothing to indicate that either the absence or presence of sericite had anything specially to do with silicosis produced by quartz, whereas the evidence incriminating dust with a high percentage of quartz was overwhelming. He explained the presence of sericite in the silicotic lungs as due to the fact that free-silica dissolves gradually in an alkaline liquid, whereas neutral silicates are much less soluble.

Contrary experimental evidence was later produced. Lemon and Higgins (32), and Fallon and Banting (33), were unable to produce lesions even remotely resembling those of silicosis by the injection of sericite into the lungs of animals.

The sericite theory is criticised, but not totally disproved, for it does at least provide an explanation for various anomalies in the chemical composition - pathogenicity relationships of some minerals.

The Freshly Fractured Surface Theory.

The idea that freshly fractured silica surfaces are especially active in the production of silicosis appears to have been first suggested by Heffernan (34) in 1935, who, following upon the work of Bragg (35) on the crystal structure of silica, suggested that its peculiar biological activity might be explained by the presence of unsatisfied valencies at the surfaces of its particles. Heffernan recognised that these valencies could be easily satisfied by hydration, and that this would occur very rapidly in any normal atmosphere. It was therefore necessary to postulate that only freshly fractured dust was active.

There was no experimental evidence in support of the theory, and even at that time there was considerable evidence against it. Gardner (36) had shown that it was possible to produce silicosis in animals by exposing them to clouds of silica dust caused by stirring up commercial ground silica. He was in the habit of buying this material in bulk and storing it for years prior to use, yet he never observed any deterioration in its power to produce silicosis. Gardner (37) was also able to produce silicosis using dusts which had previously been suspended in water for several days during particle-size grading.

The theory was again propounded by Briscoe et al. (38) in 1938 as the result of experimental studies on the physicochemical properties of finely ground material. They suggested it as a possible "explanation of the failure of attempts in the past to induce silicosis in animals by exposing them to artificially created clouds of silica dust". There are, however, other possible explanations for such failures, and any theory which purports to explain the failure of such an experiment must also explain the success of Gardner's experiments.

Although these defects in the theory were well known to many, no arguments were publicly adduced against it, with the result that it came to be accepted as true by many people.

In 1947 Policard (39) gave the following examples in favour of the theory:-

(1) North African desert sheep do not develop silicosis although continually exposed to the inhalation of sand. He stated that this was because the sand was weathered and had no unsatisfied surface valencies.

(2) Sand blasters develop silicosis through exposure to sand which,

although weathered, has freshly fractured surfaces produced by heat and impact, and is therefore dangerous.

(3) Silicosis used to be common among millstone workers. The concentration of the dust to which they were exposed was very low, but the dust was freshly generated and therefore active.

Heywood (40) pointed out that Bagnold's survey of desert sand (41) showed that it contained very few particles less than 200μ in diameter, and that air-borne dust in the desert is almost entirely non-siliceous. From this it can be readily understood why desert sheep do not develop silicosis.

The sand blasters are exposed to very fine particles produced by shattering, and there is no need to postulate specially activated surfaces in this case. The concentration and composition of the dust to which the millstone workers were exposed has never been investigated, and the example must be speculative.

"Freshly fractured" dust may be more active biologically than "old" dust, but it seems improbable. All available evidence suggests that hydration of the fresh surfaces occurs rapidly on exposure to the atmosphere. If the dust reaches the alveoli in an active state, wetting by the alveolar fluids will presumably destroy its activity instantly. When it is remembered that the time required for the production of silicosis in even the smallest animal is a matter of weeks, the importance of such a transient property would appear to be small. Also, in any working conditions (e.g. in a coal mine), the freshly fractured dust in any cloud that is caused by drilling or blasting will be accompanied by much "old" dust raised from the surroundings by the blast.

Although there are these objections to the theory, many workers believe that the freshly fractured nature of the dust is of importance in the production of silicosis.

Atomic Oxygen Theory.

In 1949, Weyl (42) demonstrated that the surface of silica exerts a strongly oxidising effect, comparable with that of ozone. The effect is very strong for dusts of freshly ground-quartz, clay, silica gel, and some other silicates, and persists in presence of moisture. The effect is enhanced by light and heat, and is proportional to the surface area of the dust.

Weyl used 4:4':4"-(dimethylamino) triphenylmethane to demonstrate the effect. This is a very sensitive reagent for atomic oxygen, forming the intensely coloured Crystal Violet. The formation of Crystal Violet can be observed by exposing the vapours of the reagent to silica or clay at 150°C., or by contact of the colourless solution of the reagent in benzene with silica gel at room temperature.

Weyl believes that this gives a plausible explanation of the toxicity of silica and clay dusts in the lungs, and that the efficiency of aluminium metal therapy is explained by the fact that aluminium is a reducing agent.

This theory is similar to the freshly fractured surface theory in that the existence of atomic oxygen is a transient phenomenon, and the assumption that freshly fractured surfaces are the only active ones is essential to Weyl's theory.

Again, the phenomenon is much more marked in the case of clay, and Weyl fits this to his theory by assuming that clay can cause silicosis. Clay does not, in fact cause silicosis, but may even prevent it (43).

The Carbon Dioxide Theory.

Edge (44) examined specimens of quartz from mining areas where silicosis is prevalent, and found that the quartz of these regions carries liquid inclusions, while that of the silicosis-free areas carries very little. The liquid inclusions were identified as liquid carbon dioxide and water or some aqueous solution.

If a piece of "milky" quartz is heated to body temperature (37°C.) it will be 60° above the critical temperature of the carbon dioxide. The pressure within the cavities will then be in the region of half-a-ton per square inch. If the containing quartz wall were broken, the carbon dioxide would expand to 400 times the volume which it occupied in the quartz.

Edge speculates as to the effect of the disintegration of the quartz particles in the lungs, and the sudden discharge of their gases under pressure into the surrounding tissue. He did not make any claim as to the importance of the liquid inclusions in quartz in the production of silicosis, but it is obviously a factor which adds further complication to the elucidation of the mechanism by which silicosis is produced as the result of the entrance of small particles of silica into the lungs.

These, then, are the theories of silicosis. None of them is completely satisfactory. All have their critics and their supporters. It is probable that no single theory will be able to explain how silicosis is produced, but that some complicated combination of mechanisms is involved.

The Unique Properties of Silica.

Silica has several properties which make it unique among industrial dusts. These properties are enumerated below.

1) Silica, when injected into any animal tissue, produces a series of pathological changes culminating in fibrosis (3). No other mineral which has so far been investigated is capable of causing such changes.

2) These effects are dependant upon the particle size. In order to produce these effects, the average diameter of the silica particles must lie between 3μ (3×10^4 Å) and 0.02μ (100 Å) (37). The upper limit is well established, but the lower limit is not. Silica particles of colloidal dimensions are very toxic (3), and produce an acute inflammatory

reaction similar to that produced by other minerals.

3) This property is a function of the surface of the particle because:-

(a) It is only shown by particles of less than a certain size.

(b) Within the fibrogenic particle size range, the effect of a given weight of silica is proportional to the fineness of the material.

(c) The pathological changes are evidently produced without any loss from the dust causing them.

(d) By preventing contact of the dust surface with the tissue (e.g. by coating with aluminium or ferric oxide) the pathological changes can be inhibited.

4) Silica has the property of facilitating the growth of tubercule bacilli in animal tissue, a property shown by no other necrotising substance.

5) The biological activity of silica has never been shown to be present in tissue culture (45).

6) Clelland (46) has demonstrated the existence of a "high-solubility" or "disturbed" layer on the surface of silica dusts.

These are the unique properties of silica. In the past only substances of industrial importance have been investigated, and some material of similar properties may occur among the less common compounds.

Prevention of Silicosis.

Since there is no known cure for silicosis after it has developed, prevention is the only effective measure.

There are several methods of prevention, none completely satisfactory, but used in conjunction they provide an effective safeguard against silicosis.

Hatch (47) considers the following to comprise a well-balanced industrial dust-control programme:-

1) Medical examination of the workers before employment to eliminate those with respiratory disorders.

2) Dust control within industry, and regular checks on its efficiency by dust surveys and medical examinations.

3) Limiting the frequency and duration of exposure of employees to dust.

In addition to these methods, the use of face masks is advocated in some industries.

The work of Denny, Robson, and Irwin (28) led to "aluminium therapy", i.e. the exposure of workers to clouds of fine aluminium pwder, the inhalation of which would have a modifying effect on the action of any silica previously inhaled.

Conclusion.

This introduction has surveyed some aspects of the silicosis problem in modern industry. The mechanism by which silicosis is produced is as yet unknown. The work described in this thesis was begun with the object of investigating some aspects of the chemistry of silica and its surface properties, relevant to the general problem but as yet almost or completely unstudied.

On consideration of all the factors discussed above, it was decided that the following subjects would make interesting and useful topics for study:-

1. The "ageing" of siliceous dusts.
2. Comparison of relevant properties of silica with the corresponding properties of closely analogous materials.
3. The effect of trace impurities on the surface properties and pathogenicity of silica.

Section 1. The Ageing of Siliceous Dusts.

Introduction.

Several workers have observed alterations in the properties (principally the solubility) of siliceous dusts as the age of the dust increased. Denny, Robson, and Irwin (26) claimed that experimental silicosis was more readily produced by exposing animals to freshly ground quartz than by exposure to stale dust. Briscoe, Matthews, Holt, and Sanderson (38) showed that freshly ground minerals were more soluble (i.e. with respect to silica) than those which had been stored for some time in bottles. Kitto and Patterson (48) found that the rate of solution of quartz decreased with the time which had elapsed since grinding, but that after two or three days any further decrease was slow.

More recently, Clelland (46) has shown that the solubility of Lochaline sand decreases on storage. His results show a decrease in solubility from 0.58 to 0.32 mg. SiO_2/100 ml. for acid-treated dust, and from 0.34 to 0.19 mg. SiO_2/100 ml. for untreated dust. These changes represent a decrease of 45% of the initial solubility over a period of seven weeks. Similarly, Gibb (49) noted a decrease in the solubility of quartz dust with storage time.

The work described here was designed to investigate this phenomenon.

Experimental.

1) General.

When considering this problem, for the reasons outlined below, the dusts must be divided into two categories:-

(i) Lochaline sand.

(ii) Quartz, Vitreosil.

Lochaline sand shows a decrease in solubility on ageing. In the course of preparation it is not subjected to any vigorous crushing or grinding action, which grinding would permit the ageing to be explained as a gradual reversion of an amorphous layer (caused by crushing) to a crystalline or semi-crystalline form. Some other explanation must therefore be sought for this. (The Lochaline sand is washed at its source; and in this process, and in the processes of sedimentation, acid-extraction, and washing, it may undergo some slight polishing through the rubbing of the particles against each other.)

Quartz and Vitreosil on the other hand are subjected to crushing and grinding in the course of their preparation for experimental work, and the crystalline change explanation may be advanced for these cases.

Any explanation which is advanced for Lochaline sand must apply, to some extent, to the other materials, since they are subjected to the same acid-extracting, washing, and drying treatment as the sand.

It is possible that the change in solubility with age of these materials is a result of several factors acting together. The following factors have been considered:-

1) The adsorption of atmospheric gases by the dusts.

2) A change in the crystalline nature of the surface of the dust after grinding.

3) The adsorption of atmospheric water vapour by the dusts.

4) The effect of other preparatory processes (acid-treatment, washing, drying).

5) The effect of absorption, by the solvent, of carbon dioxide from the atmosphere.

The experiments were conducted with the materials to which the factor being investigated was most likely to apply.

2) Preparation and Source of Materials.

The dusts used in this work were prepared from the following three siliceous materials, and are identified in subsequent sections of the work by the letters quoted in parenthesis (e.g. R.C. = rock crystal), followed in some cases by a number referring to a particular experimental batch.

(i) Rock Crystal. Large crystals of Madagascar quartz, selected for their visual purity, were reduced to dust in a steel jaw-crusher and an 8" Christy-Norris laboratory hammer-mill. The products were separated by sieving into 50-70 and 70-90 mesh B.S. fractions. Metallic contamination of the dusts during these processes cannot be avoided, and they are therefore subsequently cleaned by extraction with concentrated hydrochloric-acid, washed free of acid, and dried at 100°C. for 24 hours, giving R.C.1. (50-70 mesh) and R.C.2. (70-90 mesh): Silica content 99.92% (±0.02%).

(ii) Silica sand. A high-grade silica sand from the 40-foot Upper

Greensand bed at Lochaline in Argyllshire was used. A typical sample as received contained *ca.* 99.6-99.7% silica, and *ca.* 0.2% alumina, with traces of iron oxide, magnesia, titania, and vanadia. Fractions of the desired particle size were prepared, without grinding, by sedimentation from water. This gives Lochaline sand dusts (LAS): silica content 99.85% (±0.03%). The silica content of the dusts can be further enhanced by removal of some of the contaminants by extraction with concentrated hydrochloric-acid. This gives dusts in which the silica content depends on the degree of acid treatment.

(iii) *Fused amorphous silica.* Translucent Vitreosil, a commercial product (50), was ground in an 8" Christy-Norris laboratory hammer-mill and sieved, the 50-70 and 70-90 mesh B.S. fractions being retained. These products were cleaned with concentrated hydrochloric-acid, washed free of acid, and dried at 100°C. for 24 hours. This yielded Vitreosil dusts VTL.1 (50-70 mesh) and VTL.2 (70-90 mesh): silica content 99.8%.

3) Conditions of Solution.

The amount of silica dissolved from any dust depends on several factors. These are:-

(i) The time of contact of the dust with the liquid phase.
(ii) The specific surface area of the dust.
(iii) The pH of the solvent.
(iv) The temperature.
(v) The mass-to-liquid ratio of the dust and solvent.

In order to maintain an analogy with *in vivo* conditions, all solubility experiments were carried out at 37°C. (normal body temperature). The pH of the lung fluids is 7.5, and a borate buffer of this pH was used as solvent. To avoid contamination of the solutions by dissolved glass Lusteroid (cellulose acetate), tubes were used in all solubility experiments.

The solid and liquid phases were separated by decantation for the larger, quick-settling particles, and by filtration through a Ford Sterimat Grade SB filter pad for the very fine particles.

The quantitative estimation of silica in the solution was carried out by the molybdenum blue method. (For details of the method of analysis and composition of the reagents, see Appendix 1.).

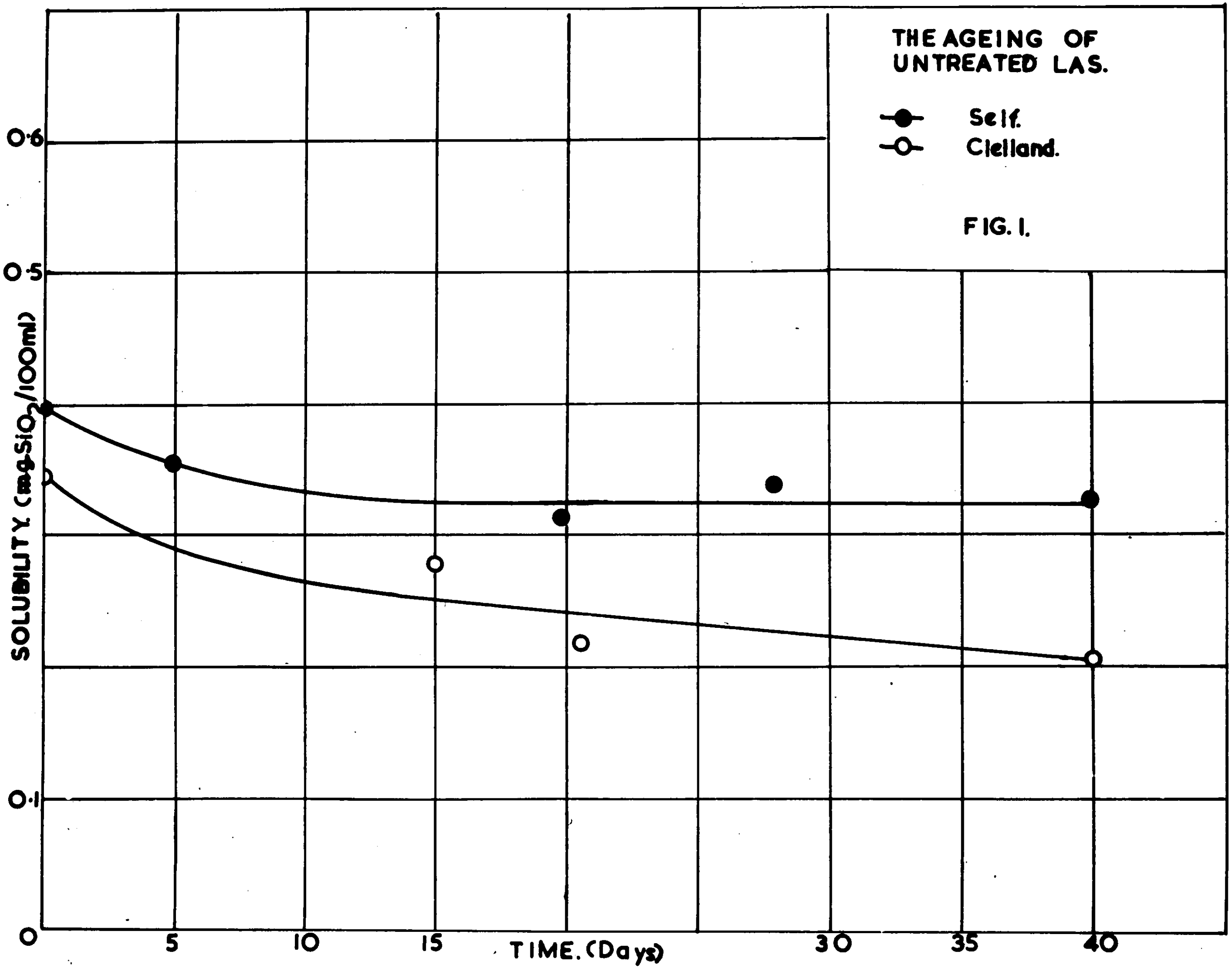
4) Discussion of Results.

(a) Initial Tests.

The initial tests were intended to confirm Clelland's results (46) on the ageing of Lochaline sand. The sand used was prepared by sedimenting twenty times from water and drying for 24 hours at 120°C. (LAS.1). Some of this LAS.1. was treated with conc. HCl until fresh acid on addition remained colourless. This sand was then washed free of acid and dried at 120°C. for 24 hours. This gave LAS.1. (E).

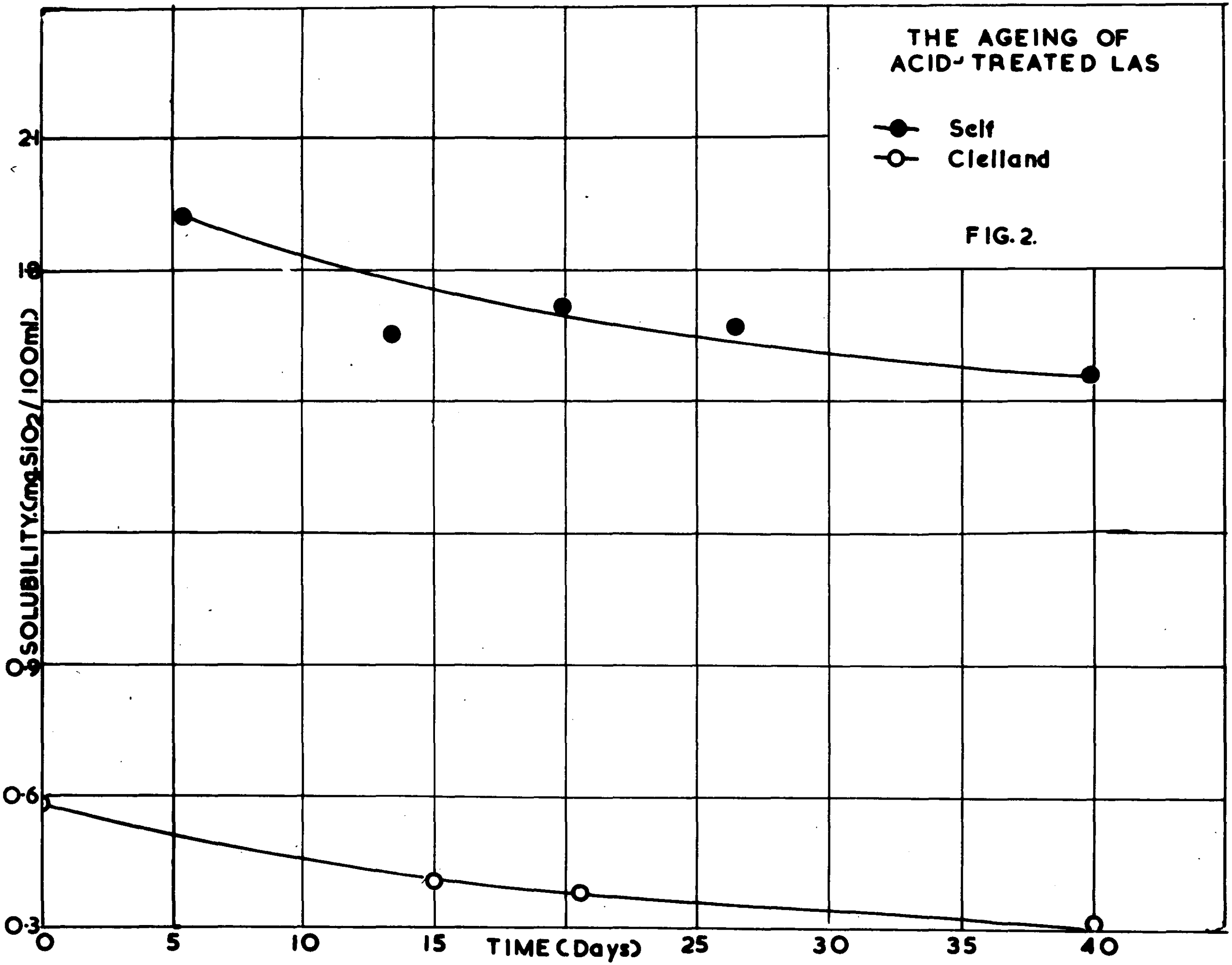
Solubility tests were carried out on these dusts at regular intervals over a period of 40 days. The results are shown compared with Clelland's in Figs. 1 and 2, and summarised in Table I.

From Table I and Figs. 1 and 2, it can be seen that the general shape of the graphs is similar, but that the levels of solubility and the percentage change in solubility on storage are considerably different. This is probably due to the use of different batches of sand, and their preparation by different workers.



THE AGEING OF UNTREATED LAS.

FIG. I.



THE AGEING OF ACID-TREATED LAS

FIG. 2.

TABLE I.

24 hour solution period at 37°C.

Mass:Liquid ratio is 4 gm. dust:40 ml. borate buffer. (pH 7.5)

LAS.3.(U) - untreated LAS (Clelland)
LAS.1. - untreated LAS (self)
LAS.3.(E) - acid-treated LAS (Clelland)
LAS.1.(E) - acid-treated LAS (self)

Dust	Solubility initially mg. SiO_2/ 100 ml.	Solubility at 40 days. mg. SiO_2/ 100 ml.	Decrease	% Decrease
LAS.3.(U)	0.35	0.21	0.14	40.0
LAS.1.	0.40	0.33	0.07	17.5
LAS.3.(E)	0.58	0.33	0.25	43.0
LAS.1.(E)	1.92	1.56	0.36	18.8

Percentage reduction =

$$\frac{\text{Initial solubility - solubility at 40 days}}{\text{Initial solubility}} \times 100$$

The experimental error of the method of analysis is ±2% (see Appendix 1).

(b) Adsorption of Atmospheric Gases. (other than water vapour)

Freshly prepared Vitreosil, quartz, and Lochaline sand were stored in atmospheres of CO_2, N_2, O_2, and air, and under vacuum. The gaseous atmospheres were obtained by evacuating the stock-bottles containing the dusts, attaching to a source of the gas, and allowing the gas to leak into the evacuated bottle.

The results obtained in these experiments were very erratic. Only the results for a batch of acid-treated Lochaline sand are shown here (Fig. 3). The graphs of solubility vs. storage time for each group showed a decreasing trend.

These experiments required the preparation of very large quantities of each of the dusts, and the erratic results may be due to lack of homogeneity of the dusts, caused by unequal distribution of the acid and wash water throughout the bulk of the dusts. This seems to be borne out by the fact that in further experiments, in which much smaller quantities of the dusts were required, fairly consistent results were obtained.

(c) Change in the Crystalline Nature of the Surface of the Dust after Grinding.

D'Eustachio and Brody (51) showed that, when a series of X-ray powder photographs of a freshly crushed mineral were taken, successive photographs showed a progressive change. Individual spots sharpened, diffuse portions of powder rings disappeared, and the number of spots increased markedly with time. They interpreted this as due to the

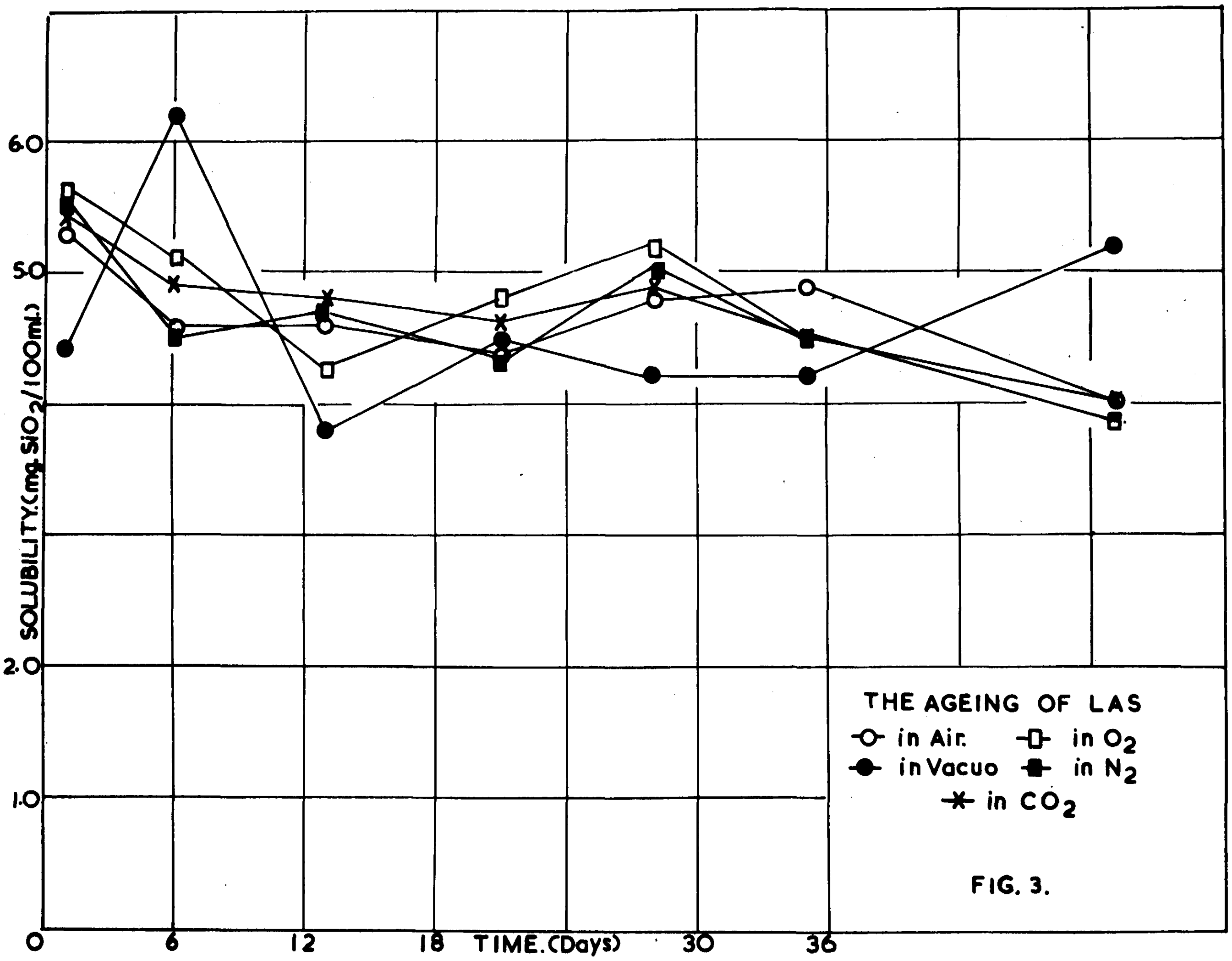

THE AGEING OF LAS
in Air.
in O2
in Vacuo
in N2
in CO2
SOLUBILITY.(mg. SiO2/100ml.)
6.0
5.0
2.0
1.0
0
6
12
18
TIME.(Days)
30
36

FIG. 3.

gradual formation of crystallites from a highly stressed surface layer.

The present work aimed at repeating the X-ray diffraction work of D'Eustachio and Brody, in the hope of correlating change in diffraction pattern with change in solubility as measured in two series of concurrent tests.

Quartz and Vitreosil were used in these experiments since they are subjected in preparation to vigorous crushing and grinding.

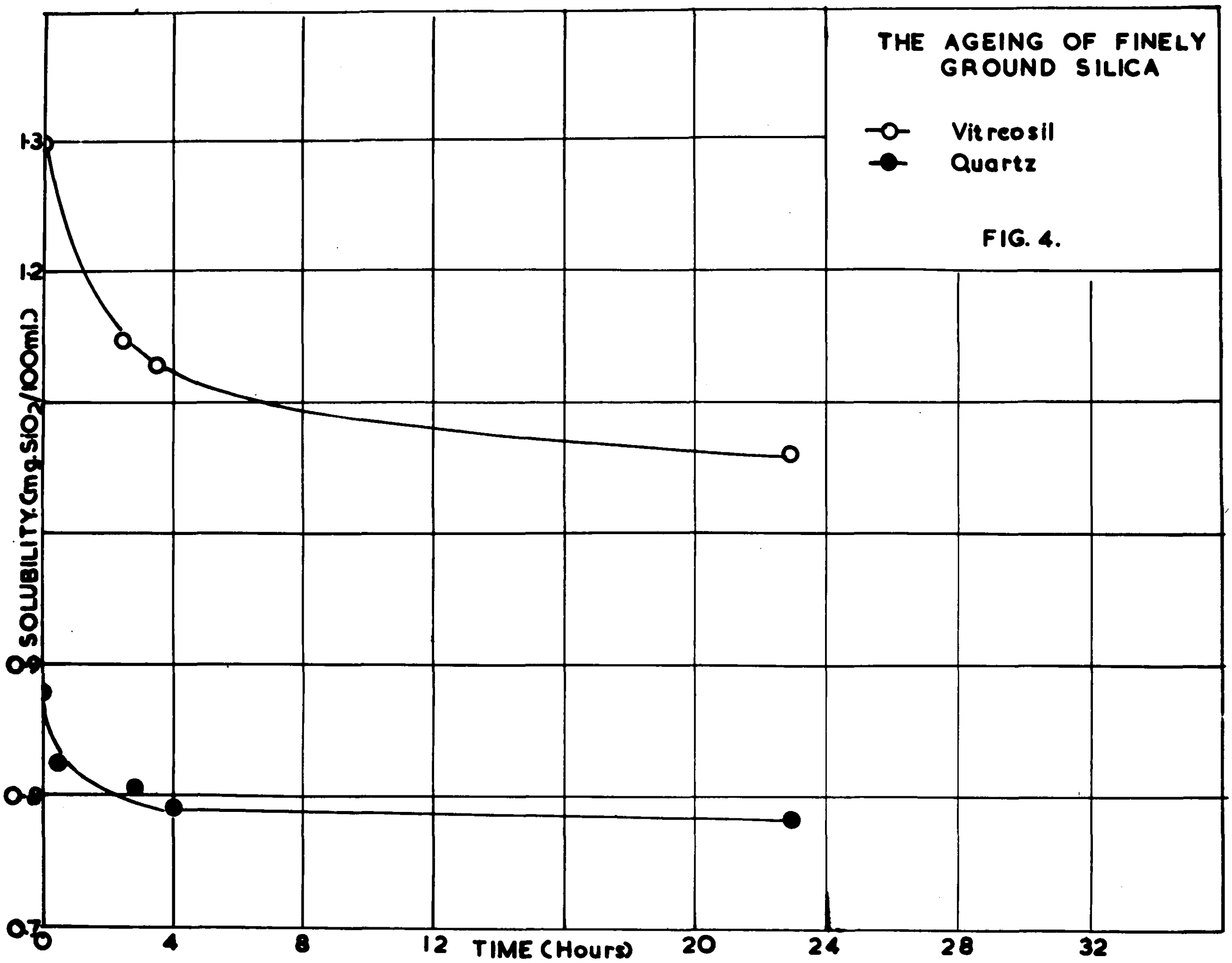
50-70 mesh B.S. dust (10 g.) (R.C.1. and VTL.1.) was crushed in a mechanical agate mortar for one hour. The average particle size of the dust thus produced was 8 μ. A small portion of this dust was used for the X-ray diffraction studies. The remainder was used for the solubility tests.

Solubility tests:-

For these tests, a mass:liquid ratio of 1 g. dust:40 ml. borate buffer was used, and the solution period was one hour. Tests were carried out at intervals over a period of 24 hours. The results for the two dusts are shown in Fig. 4. The solubility of both dusts decreases, and has reached a steady value by 23 hours. The reduction in solubility is 17.1% for Vitreosil, and 9.9% for quartz.

X-ray diffraction studies.

A sample of the dust used in the solubility tests was lightly packed into a 3/16" diameter hole in a 1/16" metal plate. The hole



THE AGEING OF FINELY GROUND SILICA

FIG. 4.

was backed by a strip of Sellotape, and the sample was cemented in place with a 10% w/v solution of ethyl cellulose in ether. The plate was then bolted in place on the X-ray set, and was not moved during the course of the run.

The photographs were back-reflection photographs, taken with copper radiation, ($K_{\alpha 1}$ = 1.54050 Å: $K_{\alpha 2}$ = 1.54434 Å) and using a nickel filter. The target to film distance was 3 cm. The machine was operated at 50 Kv. and 20 ma. The exposure time was 15 minutes and exposures were made every 30 minutes. The sample was not disturbed at all during the runs.

The photographs obtained using quartz dust are shown in Plates 1-5. The persistence of certain spots throughout all the plates (e.g. the pair indicated on all the plates) shows the lack of mechanical alteration in the sample during the run.

New spots also appear during the course of the test, and appear on all subsequent plates (e.g. the pair marked on Plate 3 which occurs 115 minutes after crushing). There is also an increase with time in the sharpness or definition of the patterns. Plates 6 and 7 are enlargements of the left side of Plates 1 and 5, and these changes can be more easily seen on them.

Identical experiments were carried out using the amorphous material, Vitreosil. No diffraction patterns were obtained for this dust. Plates 8 and 9 are the photographs obtained at 30 minutes and 23 hours

PLATES 1-3.

Back-reflection X-ray powder diffraction photographs of quartz.

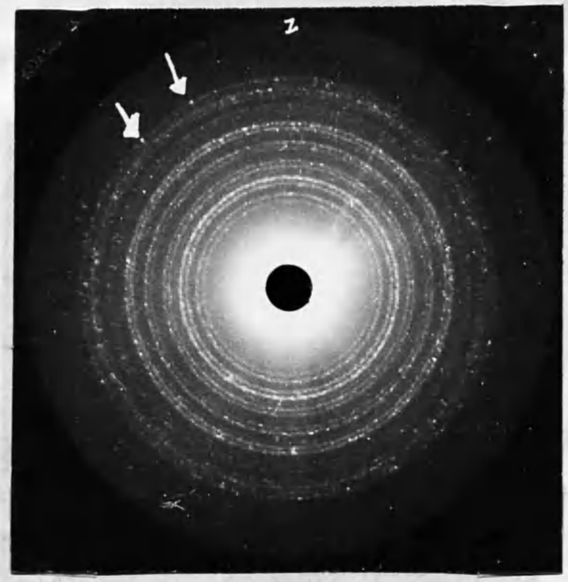


PLATE 1.

8µ quartz 20 minutes after crushing.

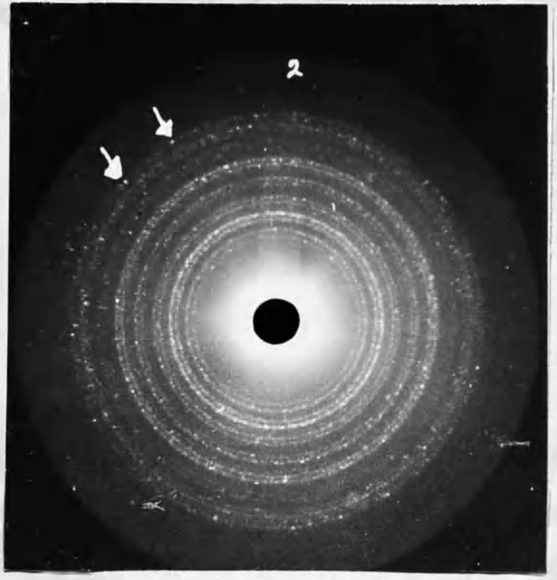


PLATE 2.

8µ quartz 39 minutes after crushing

PLATE 3.

8µ quartz 115 minutes after crushing

PLATES 4-5.

Back-reflection X-ray powder diffraction photographs of quartz.

PLATE 4.

8μ quartz 232 minutes after crushing.

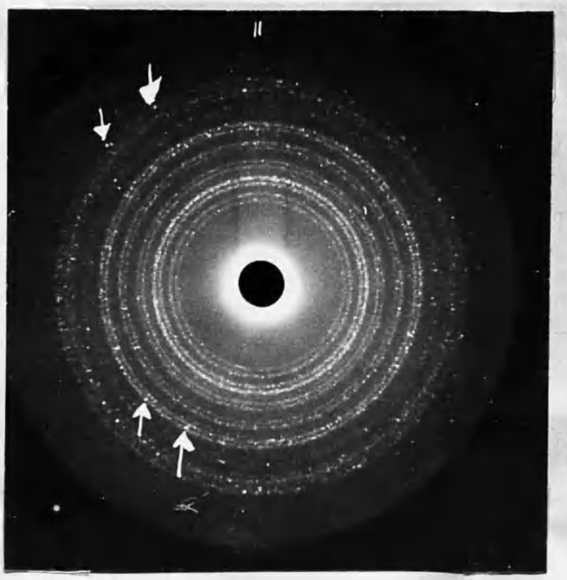


PLATE 5.

8μ quartz 474 minutes after crushing.

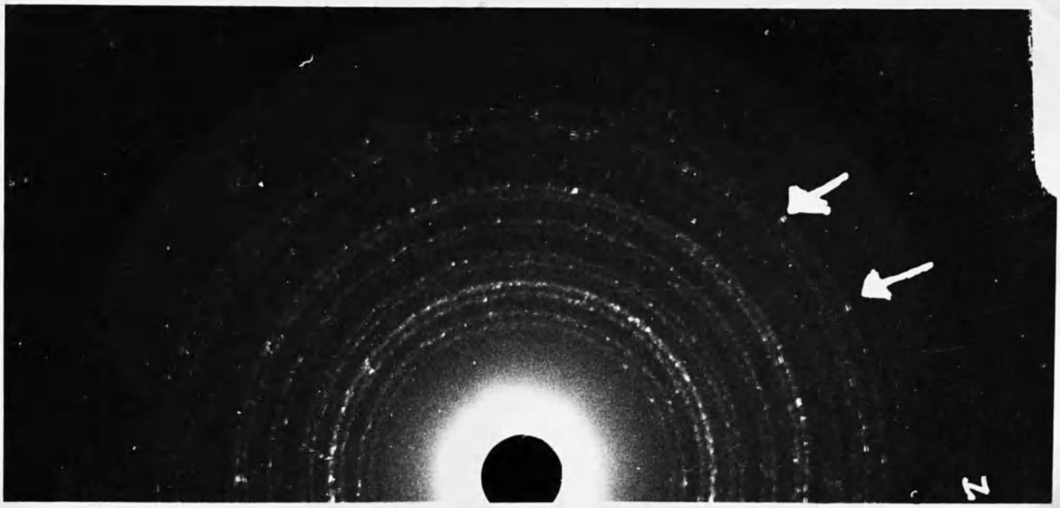


PLATE 6.

Enlargement of left hand side of Plate 1.

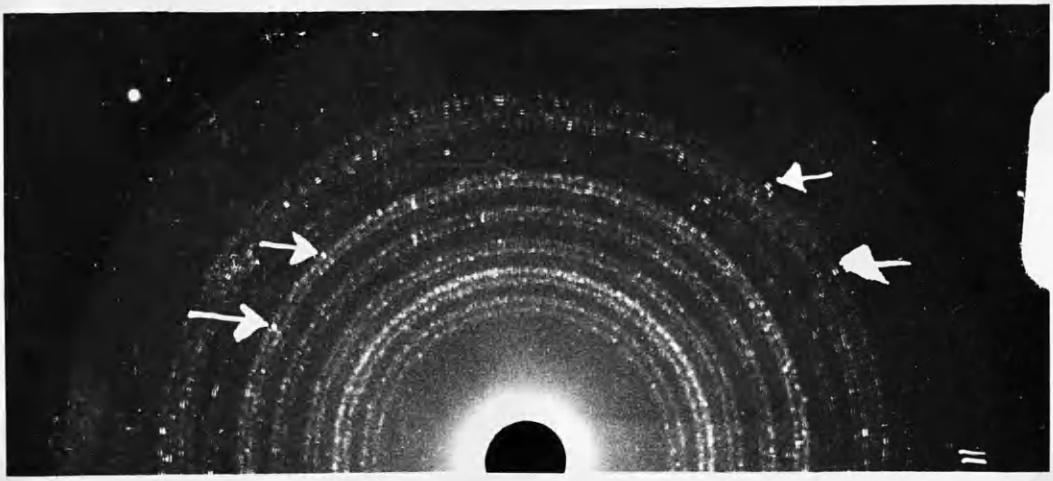


PLATE 7.

Enlargement of left hand side of Plate 5.

PLATE 8.

Back-reflection X-ray powder photograph of Vitreosil 30 minutes after crushing.

PLATE 9.

Back-reflection X-ray powder photograph of Vitreosil 23 hours after crushing.

after crushing respectively.

In the diffraction patterns obtained from the quartz many of the spots appeared as double spots. This is most readily seen in the enlarged photographs, Plates 6 and 7. This occurs in all the photographs. Similar back-reflection photographs of other oxides did not produce this effect, which is not, therefore, due to optical reflection in the photographic film. It is probably due to deformation of the quartz crystal so that one portion is reflecting at a very slightly different angle from the rest.

These alterations in the diffraction pattern of finely ground quartz can be interpreted in a similar manner to these of D'Eustachio and Brody (51). In their experiments on freshly fractured crystalline materials, they observed time-dependent changes which were tantamount to crystallisation on the surface. As an explanation they suggested that, immediately a surface was formed on a valence crystal, at least part of the surface energy is in the form of structure irregularity, and a thin, highly stressed, (possibly glassy) layer is formed. This layer is unstable and initiates recrystallisation.

The absence of change in the powder photographs for Vitreosil may be caused by the lack of crystalline nuclei in the material for the formation of crystallites.

(d) Adsorption of Atmospheric Water-Vapour by the Dusts.

The decrease in solubility on ageing might also be explained as follows:-

The dust surfaces are activated by crushing (polishing), or by acid treatment (which removes any impurities which may be present in the surface, leaving active centres), or both. The activated surfaces adsorb a large quantity of water from the wash liquids to form silicic acid. On standing in the atmosphere, the adsorbed water is gradually lost until an equilibrium with the moisture in the atmosphere is reached. This would involve dehydration of the surface silicic acid, and would result in a decrease in solubility. If the humidity of the storage atmosphere is very variable, this might lead to erratic solubility values.

The following experiments were designed to investigate the effect of the humidity of the storage atmosphere on the ageing of siliceous dusts. Freshly prepared, acid-extracted Lochaline sand was used in these tests. The natural Lochaline sand contains impurities, and on acid treatment may be expected to yield more "activated sites" for the adsorption of water than Vitreosil or quartz. Any theory applicable to Lochaline sand should also be applicable to Vitreosil and quartz.

Lochaline sand was sedimented from water until all the fine material had been removed. The dust was then treated with concentrated hydrochloric acid, until addition of fresh acid produced no further discoloration. It was then washed free of acid and dried for 24 hours at 120°C. This was then weighed out in 4 g. lots into Lusteroid tubes, and redried for 1 hour at 40°C. under vacuum. The tubes were then divided into three groups, and stored as under:-

Group 1. - Phosphorus pentoxide desiccator.

Group 11. - Desiccator containing a saturated solution of ammonium chloride (over solid ammonium chloride) giving a relative humidity of 78% at room temperature.

Group 111. - In lightly stoppered tubes.

Solubility tests were carried out on these dusts at weekly intervals over a period of eight weeks. The mass:liquid ratio was 4 g. SiO_2:40 ml. borate buffer, with a solution period of 48 hours.

The results are shown in Fig. 5.

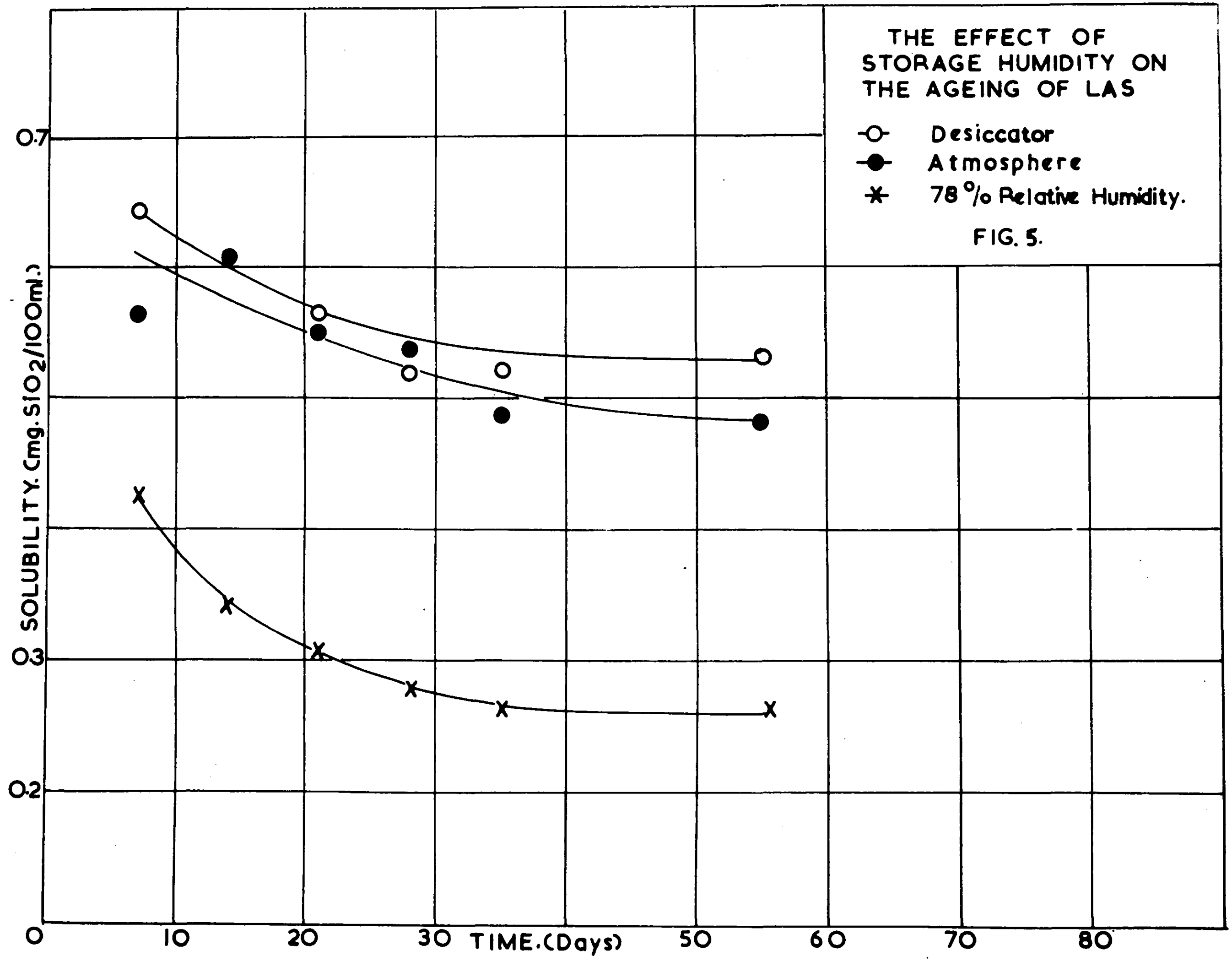
The following observations were made:-

(a) The order of solubility level was the reverse of that expected; i.e. the dust stored in the atmosphere of 78% relative humidity had the lowest solubility values, and that stored under the driest conditions the highest.

The dehydration of silicic acid would leave silica in an amorphous form, which has a higher solubility than the crystalline. The greater dehydration of the dust in the lower humidity atmosphere would leave more amorphous silica, and give a higher solubility.

(b) The experimental results for the dust stored in the most humid atmosphere were more consistent than those for the other dusts.

(c) The gradient of the graph of solubility <u>vs.</u> time for the dust stored in the most humid atmosphere was greater than the gradients



THE EFFECT OF STORAGE HUMIDITY ON THE AGEING OF LAS

FIG. 5.

of the other two, over the initial period. There is less difference between the humidity of this desiccator and the wet conditions of preparation of the dusts than in the other two cases.

(e) The Effect of Other Preparative Processes.

The graph of solubility *vs.* age of Lochaline sand (Fig. 4) has logarithmic characteristics, the solubility at zero time tending to infinity. It appears, therefore, that the method preparation of the dust produces in it a temporary condition in which it has a high solubility. The slow reversion of the dust to a form which has a lower solubility produces the ageing effect.

To investigate this, the following experiments were carried out:-

Two batches of Lochaline sand were prepared:-

LAS.1. - Lochaline sand was sedimented twenty times from water, and dried for twenty-four hours at 120°C.

LAS.1.(E). - Lochaline sand was sedimented twenty times from water. It was then extracted with concentrated hydrochloric acid until the addition of fresh acid produced no further colour. It was washed free of acid, and dried at 120°C. for twenty-four hours.

These dusts were allowed to age in the atmosphere for forty days. Solubility tests were carried out at weekly intervals. The dust remaining after forty days was separated into batches for "repreparation" (i.e. retreatment with acid, rewashing, and drying) thus:-

LAS.1. - The unused LAS.1. was divided into two lots, one of which was washed and dried, giving LAS.1(A), and the other dried only, giving

LAS.1(B).

LAS.1.(E). - The unused LAS.1.(E) was divided into three batches and retreated, giving the following dusts:-

LAS.1.(E)A. - retreated with concentrated hydrochloric acid, washed and dried.

LAS.1.(E)B. - washed and dried.

LAS.1.(E)C. - dried only.

The solubility tests were then continued with these dusts. The results are shown in Fig. 6 and 7.

The solubilities of the dusts after this "repreparation" were in the following order:-

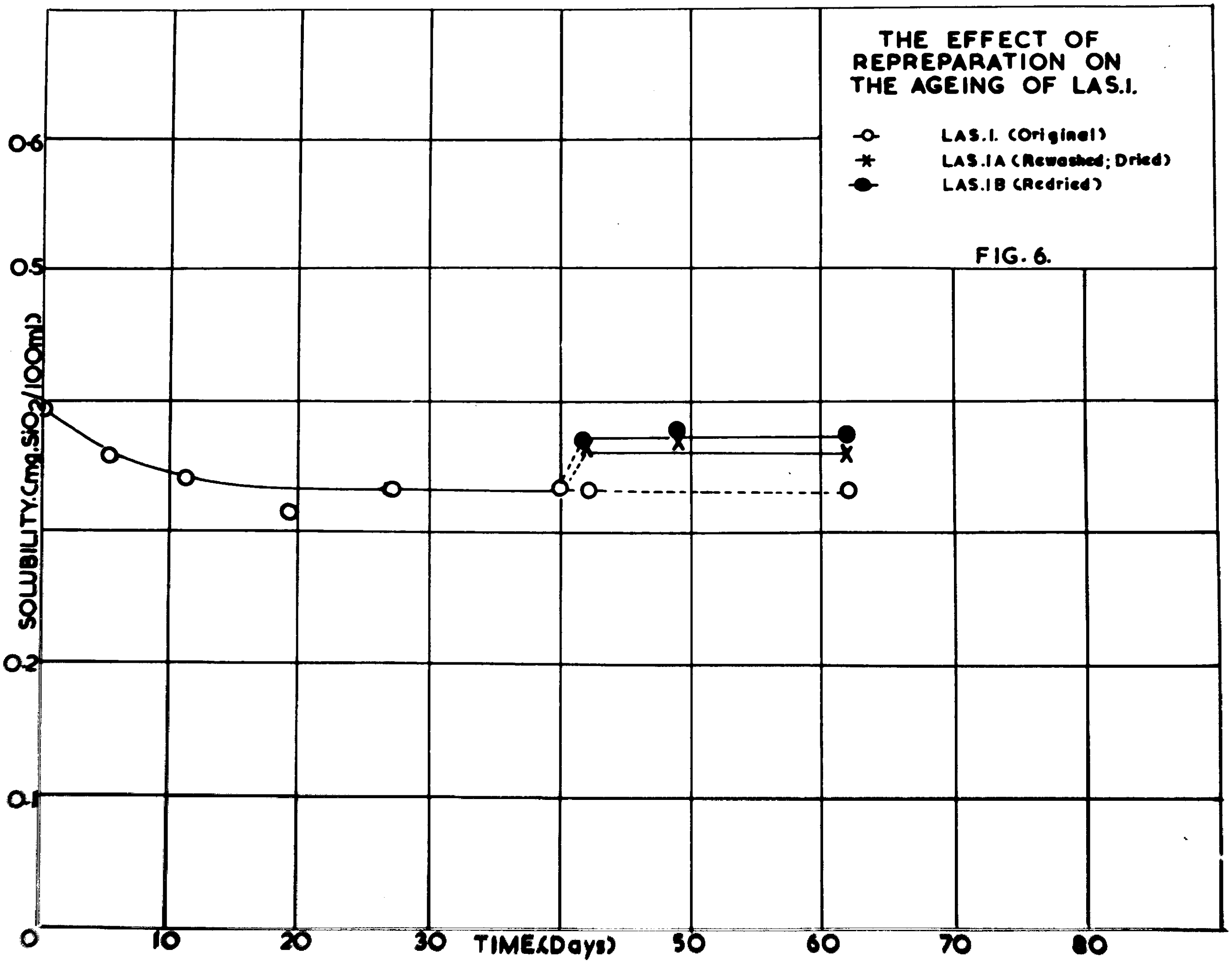
LAS.1(B) ∠ LAS.1(A).

LAS.1.(E)A ∠ LAS.1.(E)C ∠ LAS.1.(E)B.

If the factor which causes the decrease in solubility on ageing (or perhaps more accurately a temporary increase in solubility which decreases to a true value) had been introduced in the preparatory processes, it would be expected that the "repreparation" of the dusts would cause a further ageing effect. This was not the case. The gradients of the graphs showed no change after the "repreparation" process.

(f) The Effect of Absorption of Atmospheric Carbon Dioxide by the Solvent.

Holt (52) and Holt and Briscoe (53) have shown that carbon dioxide



THE EFFECT OF REPREPARATION ON THE AGEING OF LAS.I.

FIG. 6.

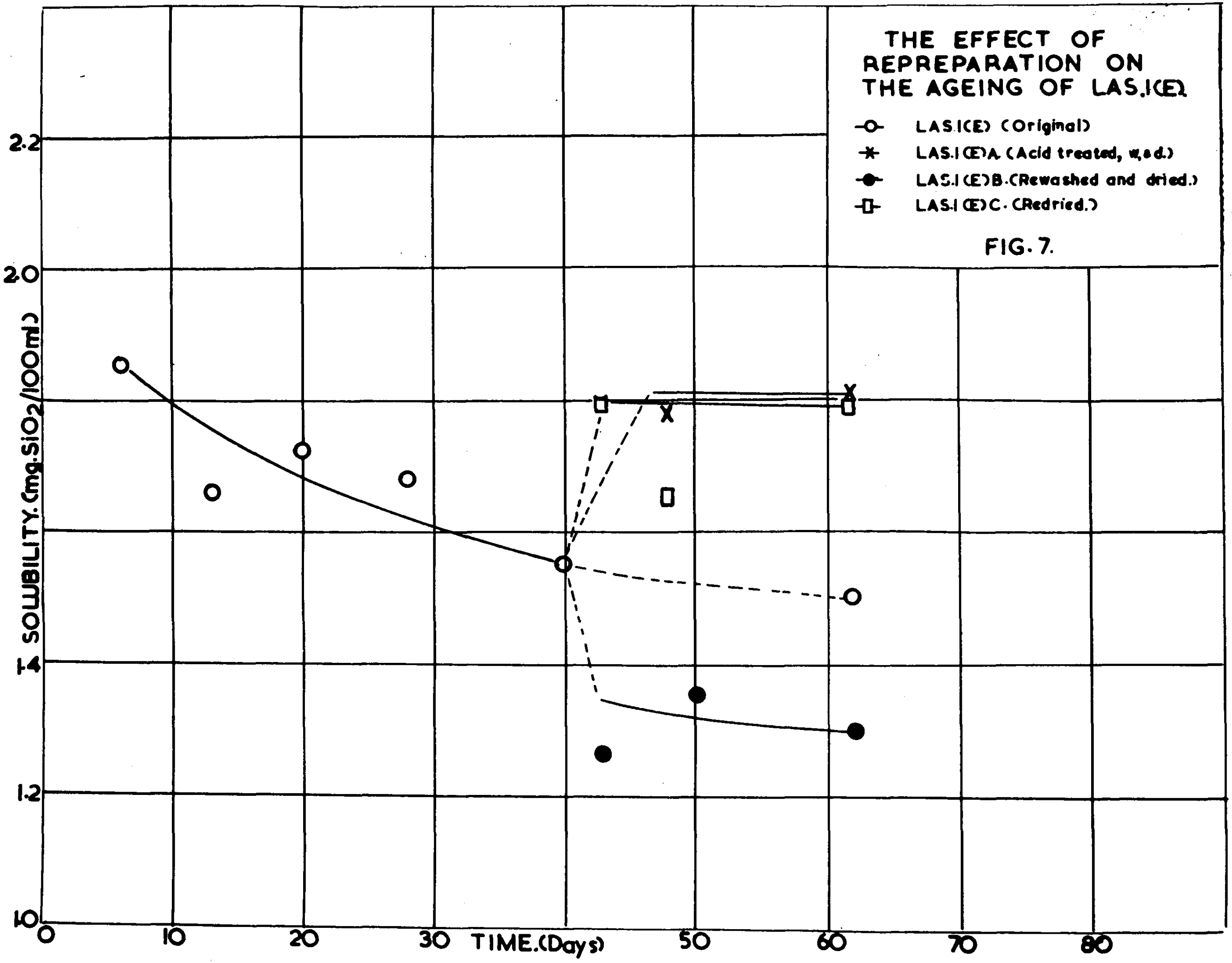


FIG. 7.

THE EFFECT OF REPREPARATION ON THE AGEING OF LAS.I(E).

has a marked effect on the solubility of cements and industrial siliceous dusts. They reached the following conclusions:-

(i) Calcium silicate is decomposed by carbon dioxide, resulting in an increase in the silica which passes into solution.

(ii) Carbon dioxide reduces the solubility of lime-free flint.

(iii) Calcium carbonate increases the solubility of flint.

The solvent for all solubility experiments carried out in this work is borate buffer (pH = 7.5) which is prepared in large quantities (20 litres). This is stored in an aspirator where it may absorb some carbon dioxide from the atmosphere. This would effect the results of solubility experiments.

To test this idea, carbon dioxide (from Drikold) was bubbled through some freshly prepared borate buffer solution for two hours. After 90 minutes, the pH had fallen from 7.5 to 5.6 Solubility tests were carried out on quartz and Lochaline sand using this buffer and a freshly prepared solution. The results are shown in Table II.

The results show that the absorption of carbon dioxide by the borate buffer leads to a decrease in solubility of these dusts. This decrease in solubility with decrease in pH of the solvent is in agreement with the results shown in Fig. 8.

The solvents used by other workers in the silicosis research field are also susceptible to the effect of carbon dioxide. Kitto and Patterson (48), for example, used unbuffered solutions of sodium carbonate in their work. They themselves demonstrated that, owing to absorption of carbon dioxide, the pH of their solvents dropped from 11 to 9 in two days. Further, they used milky quartz, the "milkiness" of which Edge (44) has shown to be due to carbon dioxide inclusions. The release of these carbon dioxide inclusions into the solvent by the bursting of a particle wall, previously untouched by crushing, but weakened by dissolution of silica from it, could result in further interference in solubility tests.

Briscoe and his co-workers (38) used water as a solvent. King (25) in his work used ascitic fluid (i.e. lung fluids). These may also be susceptible to the effect of absorption of atmospheric carbon dioxide.

The absorption of carbon dioxide by the solvent may be one of the factors causing the (in this case apparent) decrease in solubility of siliceous dusts on ageing. In this case, however, it is the solvent which is changing and not the dust.

In view of Edge's identification of the inclusions in "milky" quartz as liquid carbon dioxide (44), and of the high carbon dioxide content of the lungs, it is possible that carbon dioxide may play an important part in the mechanism of silicosis.

TABLE II.

The effect of absorption of CO_2 by the solvent on the solubility of siliceous dusts.

4 g. SiO_2/40 ml. borate buffer.   24 hour solution period.

	Solubility	($mg. SiO_2/100 ml.$)
	Quartz	Lochaline sand
Borate buffer	0.245	0.495
Borate buffer + CO_2	0.184	0.230
Percentage decrease	25	50

[illegible]

(1) [illegible] easily weatherable material).

(2) Etching with hydrofluoric acid (removes the disturbed layer).

(3) Mounting the crystals in a moisture free atmosphere.

General Discussion.

The problem of the alteration of the properties of quartz crystals on ageing is also encountered in the field of electronics, where it is found that there is a variation in the frequency and activity of quartz oscillator crystals over a period of time. The amount of ageing is determined by the method of finishing the crystals. The ageing has been explained thus (54):-

"Lapping produces a distrubed layer from which some particles break away completely. Some cracking also occurs which does not result in break-off of particles. The result is a surface with a large number of cracks giving a non-homogenous layer. When this layer is exposed to moisture, a weathering action takes place. Much of the material contiguous to the cracks falls off, and the frequency of the crystal rises".

Methods for preventing or reducing the ageing of quartz crystals for electronic work are as follows (54, 55):-

(1) Scrubbing with a brush and soap and water (removes much of the easily weatherable material).

(2) Etching with hydrofluoric acid (removes the disturbed layer).

(3) Mounting the crystals in a moisture free atmosphere.

(4) First, rough adjustment to their approximate frequencies, and then heat-ageing in an oven which subjects them to several heating-cooling cycles between 240°F. and 75°F. The units are then mounted in cages and again aged.

The fact that the crystal can be stabilised by a heating-cooling cycle suggests that in the ageing process some change in the nature of the surface is involved, the heating-cooling cycle resulting in a stable crystalline form in the surface material.

If the exposure of the 50-70 mesh dusts used in the experiments resulted in the break-off of fine material, these fines would be carried off in suspension in the wash water of the acid. This, in addition to the removal of impurities by acid treatment, would provide "active" surfaces for the adsorption of water.

The factors given for the ageing of quartz crystals in electronic work are, therefore, in agreement with those which this work has suggested as causing the decrease in solubility of siliceous dusts on ageing.

Conclusions.

On the basis of these results, the reduction in solubility of siliceous dusts on ageing may be visualised as the combined effect of a number of factors, their relative importance varying according to the characteristics (particle size, degree of purity, etc.) of the material.

These factors are as follows:-

(1) A change in the nature of the surface of the dusts from a highly vitreous to a less vitreous state. This factor is of importance for very fine dusts, but is of less importance for (say) 50-70 mesh dusts.

(2) The effect of moisture adsorbed at the surface of the dusts and the humidity of the atmosphere. The factor is of importance in all cases.

(3) The absorption of carbon dioxide by the solvent. This produces an <u>apparent</u> ageing effect. The decrease in solubility is not due to any change in the dusts, but to deterioration of the solvent.

[illegible] a disturbed layer on the surface of the dust produced by grinding, (b) the nature of the pretreatment carried out on the dusts. This layer was also shown to affect the amount of adsorption of basic dyestuffs by the dusts. The layer can be removed from quartz and vitreosil dusts by etching with 40% hydrofluoric acid.

Since no other material has been shown to possess these propert it was decided to compare them with the corresponding properties of analogous materials. Titanium oxide (TiO_2) was chosen for this pu Both titanium and silicon belong to Group 4 of the periodic classification, titanium following silicon in the group. They did

SECTION 2.

A Comparison between the Solubility and Sorption Properties of Rutile (TiO_2) and of Quartz (SiO_2).

(a) Introduction.

In the course of research in the field of silicosis, silica has been shown to have several unique biological properties (see Introduction). Silica has also been shown by Clelland (46) to possess some peculiar solubility and sorption characteristics. He demonstrated the existence of a "high-solubility layer" on the surface of siliceous dusts, and correlated this layer with (a) the presence of a disturbed layer on the surface of the dust produced by grinding, and (b) the nature of the pretreatment carried out on the dusts. This layer was also shown to effect the amount of adsorption of basic dyestuffs by the dusts. The layer can be removed from quartz and Vitreosil dusts by etching with 40% hydrofluoric acid.

Since no other material has been shown to possess these properties, it was decided to compare them with the corresponding properties of analogous materials. Titanium oxide (TiO_2) was chosen for this purpose. Both titanium and silicon belong to Group 4 of the periodic classification, titanium following silicon in the group. They might thus be expected to show similar properties.

Titanium oxide is of interest also in that no cases of pneumoconiosis have been reported amongst workers handling the material in the very fine and very pure form in which it is used as a pigment (56).

The essence of the problem was to show wherein the properties of titanium dioxide and silicon dioxide differ and where they are similar, so that some further evidence might be gained as to the nature of the fibrogenic action of silica.

(b) General Comparison of Properties.

Both oxides occur in nature; silica abundantly as quartz, flint, and sand; titanium oxide less abundantly, but widely distributed as rutile, brookite, and anatase.

Titanium oxide is an amphoteric oxide; silica is a weakly acidic oxide.

The crystal structures of quartz and rutile (the titanium oxide chosen for this work) also differ. Quartz occurs in hexagonal prisms (trigonal system) terminating in hexagonal pyramids. Rutile is of the tetragonal crystal system.

(c) Experimental.

1. General.

To make this comparison the following properties of the dusts have been investigated:-

- (i) The variation in solubility with pH of the solvent.
- (ii) The effect of treatment with hydrochloric and hydrofluoric acids.

(iii) The existence of a "high-solubility layer" on rutile dusts.

(iv) The adsorption of dyestuffs by rutile and the effect of acid treatment upon this adsorption.

2. Solubility Experiments.

(i) Materials:- Source and Preparation of Dusts.

It was not possible to obtain natural rutile of high purity in sufficient quantities for this work. However, a crude rutile was obtained as several large (1"-2") lumps which were crushed in an 8" Christy-Norris laboratory hammer mill, and then graded by passing through screens. The particle-size distribution of the material thus obtained was very uneven, there being much large material and much very fine, but little of the 70-90 mesh B.S. fraction. The fractions 9-50 and 50-90 mesh B.S. were used in subsequent work. The average particle size of these dusts (calculated from the formula $\Sigma(nd)/\Sigma n$) was found using a microscope with a calibrated graticule. They were 589 µ and 359 µ respectively.

The dusts, which were analysed by Hagmaier's method (57), were found to contain 83.3% TiO_2. The balance was silica and iron oxides.

These dusts were washed with distilled water to remove any adherent fines and dried at 120°C. for 24 hours. This gave rutile dusts R.1 (9-50 mesh B.S.) and R.2 (50-90 mesh B.S.)

A portion of each of these dusts was treated with concentrated hydrochloric acid until addition of fresh acid produced no further discoloration. The dusts were then washed free of acid and dried at 120°C. for 24 hours, giving rutile dusts R.1(A) and R.2(A) respectively.

Further portions of dusts R.1 and R.2 were treated with 40% hydrofluoric acid for five minutes. The dusts were then washed free of acid and dried at 120°C. for 24 hours. This gave rutile dusts R.1(B) and R.2(B) respectively.

An amorphous dust (T.1) from titanium oxide (58) was also used. This dust "balled up" on storage in a jar, owing to moisture, but on suspension in an aqueous medium it gave a dust of average particle size less than 5 µ.

(ii) Estimation of Titanium in Solution.

A rapid method for estimating small quantities of titanium in solution was required for this work. A colorimetric method was the obvious choice. Among the reagents considered for this purpose were:- salicylic acid (59), gallic acid (60), and chromotropic acid (61). Most of these substances are unstable in solution. The number of interfering ions in each case is relatively large. None of these reagents has, therefore, been extensively used in the estimation of titanium.

The oldest known method of estimating titanium is that using hydrogen peroxide (62). With a solution of titanium sulphate, hydrogen peroxide produces a yellow colour (said to be due to pertitanic acid). With small amounts of titanium the colour is proportional to the amount present. The lower limit for the accurate use of this method is 1.5 mg. TiO_2/100 mg., and there are again several interfering ions.

The method eventually decided upon was that of Yoe and Armstrong (63) using the reagent sodium 1:2-dihydroxybenzene-3:5-disulphonate (Tiron) ($C_6H_2(OH)_2(SO_2ONa)_2.H_2O$) adapted to suit the requirements of this work. The reagent is sensitive to 1 part in 10^8. The tint and intensity of colour remain constant over the pH range 4.3-9.6 and Beer's Law is obeyed over the useful range of concentration.

Ferric ion interferes, giving a red colour in alkali and blue in acid solution. This latter colour can be bleached with sodium dithionite at pH 5. (Tiron can be used for the determination of iron). Oxidising agents interfere. Certain other ions consume the reagent and cause diminution in the titanium colour. This interference can be overcome in the solutions used for analysis by using a large excess of the reagent.

(iii) <u>Preparation of Reagents.</u>

The following reagent solutions were used:-

A. <u>Standard Titanium Solution.</u> Potassium titanium oxalate (4.5 g.) was placed in a Kjeldahl flask to which was added A.R. ammonium sulphate (8 g.) and concentrated sulphuric acid (150 ml.). The mixture was boiled, at first gently and then briskly for ten minutes, to remove the oxalic acid formed. The solution was cooled, diluted with distilled water, filtered, and made up to 1 litre with distilled water. The titanium oxide in this solution was estimated gravimetrically by precipitation with ammonia, ignition to TiO_2, and weighing as such. The solution was then diluted with 0.5 M H_2SO_4 to give a solution containing 4 mg. TiO_2/litre.

B. Acetate Buffer Solution. 500 ml. molar acetic acid (60 g. acetic acid = 57.2 ml. glacial acetic acid/litre) is mixed with 500 ml. molar sodium acetate (82 g. anhydrous sodium acetate/litre).

C. Tiron Solution. Sodium 1:2-dihydroxybenzene-3:5-disulphonate (4 g.) is dissolved in 100 ml. distilled water. The reagent solution is only stable for approximately 10 days, when it becomes yellow and must be discarded.

D. 3N Ammonia Solution. 213 ml. ammonia solution (S.G. 0.88) is diluted to 1 litre with distilled water.

E. 0.5M Sulphuric Acid. 28 ml. sulphuric acid (S.G. 1.84) is added to distilled water and made up to 1 litre.

(iv) Procedure for Estimation of Titanium.

To 10 ml. of unknown TiO_2 solution is added 2 ml. of reagent solution. The pH of this mixture is adjusted to 4.6 by the addition of 3N ammonia solution. (The volume of ammonia required for this was determined previously by potentiometric titration. For 10 ml. of the 0.5M sulphuric acid the volume of 3N ammonia required was 2.8 ml.) 5 ml. of the acetate buffer solution is added, and the volume made up to 20 ml. with distilled water. The yellow colour develops immediately, and the optical density of the solution is measured at a wavelength of 410 µ using an Unicam S.P. 500 photo-electric spectrophotometer.

The presence of ferric iron in these solutions produces a blue colour which can be bleached by the addition of a very small quantity of sodium dithionite. Sodium dithionite is unstable under these conditions, gradually decomposing to give a precipitate of sulphur; hence, when this reagent is used, the estimation should be carried out within 15 minutes of its addition.

(v) Calibration Curve.

A calibration curve for the Unicam S.P. 500 spectrophotometer was obtained using known dilutions of the standard titanium solution A in 0.5N H_2SO_4, and carrying out the estimation as described above.

(vi) Accuracy.

Preliminary light absorption experiments with an EEL colorimeter showed that there was no filter which would give a reading on the accurate part of the logarithmic scale of this instrument when low concentrations of titanium oxide were being estimated.

The light absorption was therefore measured using the Unicam S.P. 500 spectrophotometer with which the wavelength of the light beam can be adjusted to that giving maximum absorption (410 µ for the titanium complex). Using this instrument the accuracy was ±2%.

3. Discussion of Results.

(i) The Variation in the Solubility of Rutile with pH of the Solvent.

Rutile dust R.2 and dust T.1 were used in this work. Acid solutions to cover the pH range 0-7 were obtained by diluting the 0.5M H_2SO_4 solution E. 25 ml. of 0.5M H_2SO_4 were diluted to 100 ml. with distilled water. Successive dilutions gave solutions of increasing pH.

The pH of these solutions were measured. Since the TiO_2 must be estimated in solution at pH 4.6, the amount of 3N ammonia solution required to bring these solutions to this pH was determined by potentiometric titration. For acid solutions less than 0.05M the addition of 5 ml. of acetate buffer solution B was sufficient to bring the solutions to this pH.

Molar caustic soda solution was made up. Dilution of this provided a series of solutions covering the alkali side of the pH scale. The amount of 3N H_2SO_4 required to bring the pH of these solutions to 4.6 was also determined.

For the dust T.1 the mass-to-liquid ratio was 0.4 g. TiO_2/40 ml. solvent, and the solution period was 48 hours at 37°C.; for the dust R.1 the mass-to-liquid ratio was 1 g. TiO_2/50 ml. solvent, and the solution period was 24 hours at 37°C.

At the end of the solution period the liquids were decanted and filtered through Ford Sterimat filter pads (Grade SB). With the solutions of extreme pH (ca. 1 and 13) the first few drops to pass through the pads were discoloured yellow, indicating that something had been extracted from the filter pad. These first few drops were consequently discarded and the estimations carried out on the clear filtrates.

The results of these tests are shown in Fig. 8 along with a similar curve for quartz (64).

From these results it can be seen that the general shape of the graphs is similar. Each graph shows a minimum, that for quartz being sharp and occurring at pH 3, while those for the titanium dusts are flat and cover the pH range <u>ca</u>.3-12. The solubilities at the minimum are also different. The quartz has a solubility of 2.2 mg. SiO_2/litre at the minimum, while titanium oxide has negligible solubility in both cases. The solubility values cannot strictly be compared since the mass-to-liquid ratios and particle size distributions (i.e. the surface area of the dust in contact with the solvent) are not identical. However, a solubility value of 1.67 mg. SiO_2/100 ml. has been obtained at pH 7.5 for a fine quartz dust of similar particle size to dust T.1. Under identical experimental conditions the solubility of T.1 at pH 7.5 was too small to be detected by the method used.

This indicates that titanium oxide has negligible solubility at the pH of the lung fluids.

It was decided to carry out the remaining solubility tests in an acid medium.

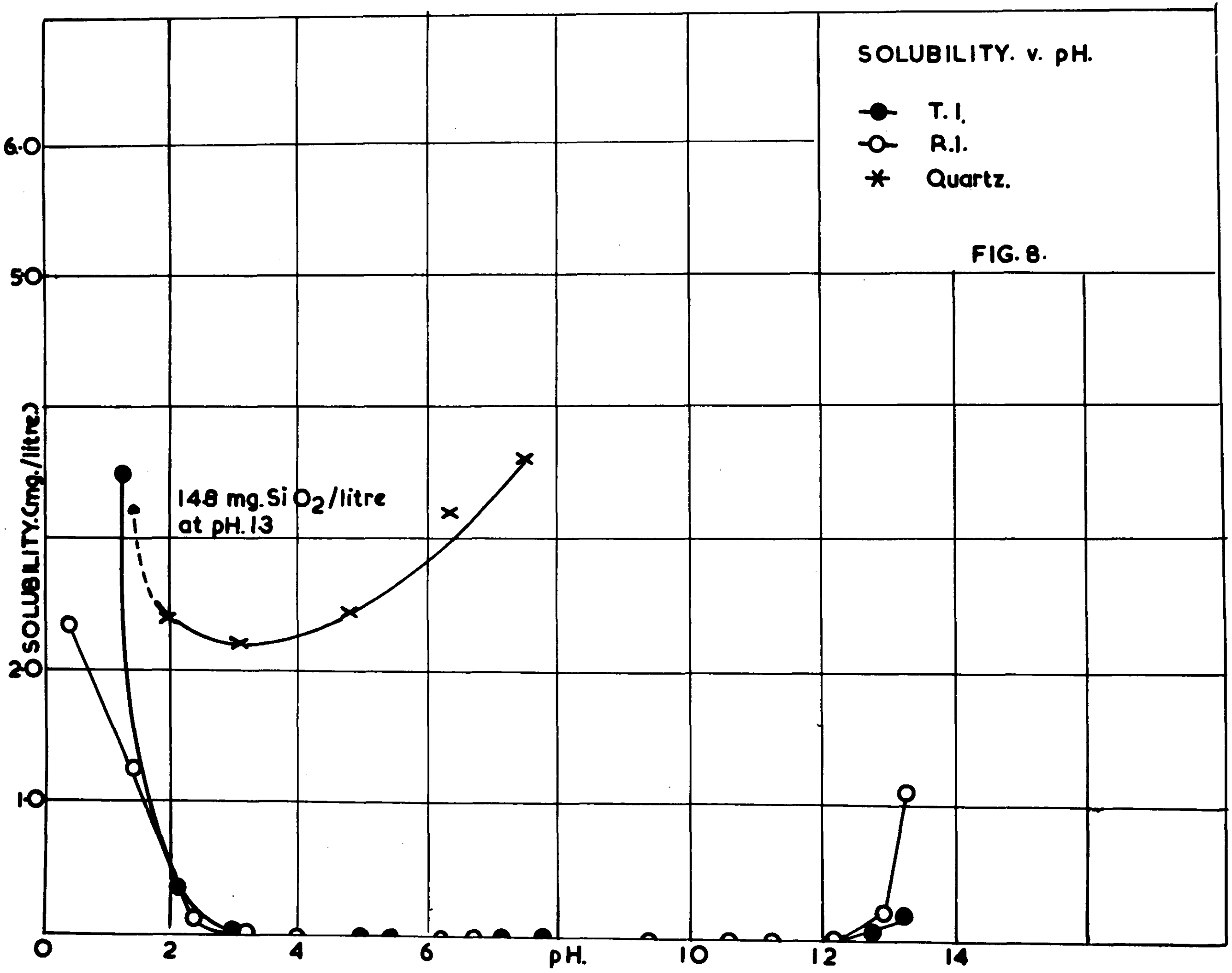

SOLUBILITY. v. pH.
T. I.
R.I.
Quartz.
148 mg. Si O_2/litre at pH. 13
SOLUBILITY.(mg./litre.)
6.0
5.0
2.0
1.0
0
2
4
6
pH.
10
12
14

FIG. 8.

(ii) The Effect of Acid-treatment on the Solubility of Rutile.

Rutile dusts R.1, R.1(A), and R.1(B) were used.

The results of these tests are shown in Table III along with similar figures (i) for quartz and (ii) for quartz which had been etched with 40% hydrofluoric acid to remove the "high-solubility layer".

For the rutile dusts a mass-to-liquid ratio of 1 g. TiO_2/50 ml. 0.5M H_2SO_4 was used with a solution period of 48 hours at 37°C.

For the quartz dust a mass-to-liquid ratio of 4 g. SiO_2/40 ml. borate buffer was used with a solution period of 48 hours at 37°C.

From these results it can be seen that whereas treatment of quartz with hydrofluoric acid results in a decrease in solubility, due to the removal of the "high-solubility" surface layer, similar treatment of rutile with hydrofluoric acid produces an almost equal increase in solubility. This is probably due to an increase in the purity of the material through removal of impurities by the acid.

Increasing the purity of the rutile by acid extraction would provide a greater surface area for solubility. This surface would be new and fresh and might be more soluble than the old surface. Further, the removal of impurities would eliminate any depressant effect of the type occurring when silica is "diluted" with aluminium and alumina (26).

TABLE III.

The Effect of Acid-treatment on the Solubility of Rutile and Quartz Dusts.

DUST	pH of Solvent	Solubility (mg./1000 ml.)	Change in Solubility (mg.)	% Change in Solubility
R.1	0.4	3.40	-	-
R.1(A)	0.4	4.02	+0.62	+18.2
R.1(B)	0.4	5.03	+1.62	+67.8
Quartz	7.5	3.5	-	-
Quartz (no HS layer)	7.5	1.2	-2.3	-65.6

time of contact with the solvent which (Fig. [illegible]) is not the case wi quartz until the "high-solubility" layer has been removed.

After twenty days the cumulative concentration of titanium oxide

(iii) (a) Investigation into the Possible Existence of a "High-Solubility Layer" on Rutile.

Rutile dusts R.1, R.1(A), and R.1(B) were used in these tests. To determine whether there is a "high-solubility" surface layer on rutile, "extractive" solubility tests were carried out.

0.5 g. of each dust was agitated for 24 hours at 37°C. with 25 ml. of 0.5M H_2SO_4 (pH 0.4). At the end of the first solution period, the solvent was carefully decanted from the dust. The dust was then washed with distilled water followed by 0.5M H_2SO_4. 25 ml. of fresh solvent were then added to the dust and the test continued. This procedure was repeated regularly for all three dusts over a period of twenty days.

The results are shown in Fig.9. Results from similar experiments with quartz taken from other work (65) by the writer are shown in Fig. 10.

From Fig. 9 it is seen that under these experimental conditions, the amount of titanium oxide dissolved is directly proportional to the time of contact with the solvent which (Fig. 10) is not the case with quartz until the "high-solubility" layer has been removed.

After twenty days the cumulative concentration of titanium oxide in the solvent was 45 mg. TiO_2/litre, while that for quartz was 15 mg. SiO_2/litre.

If, therefore, a high-solubility layer is present on the surface

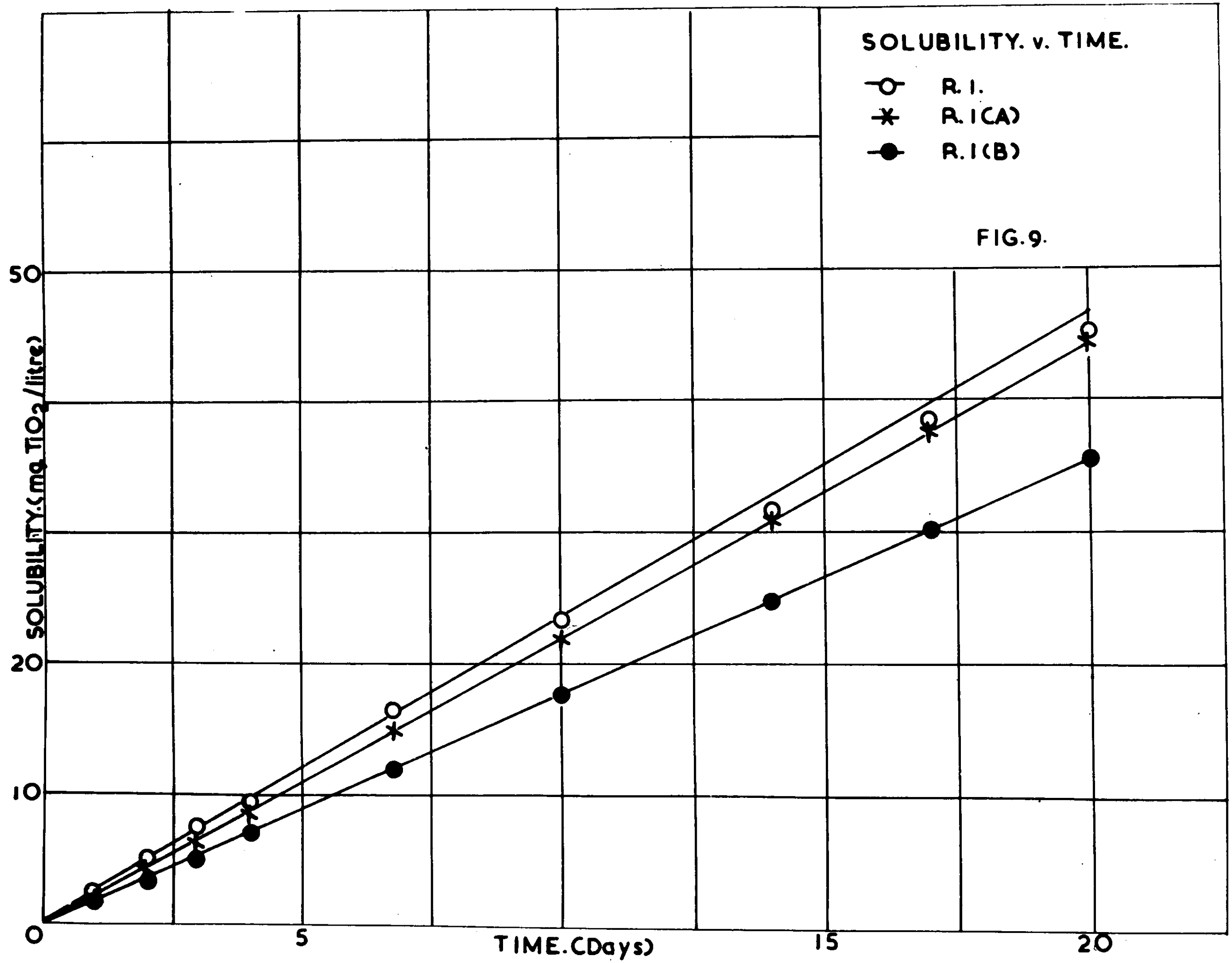

SOLUBILITY. v. TIME.
R. I.
R. I (A)
R. I (B)
SOLUBILITY. (mg. TiO$_2$/litre)
50
20
10
0
5
15
20
TIME. (Days)

FIG. 9.

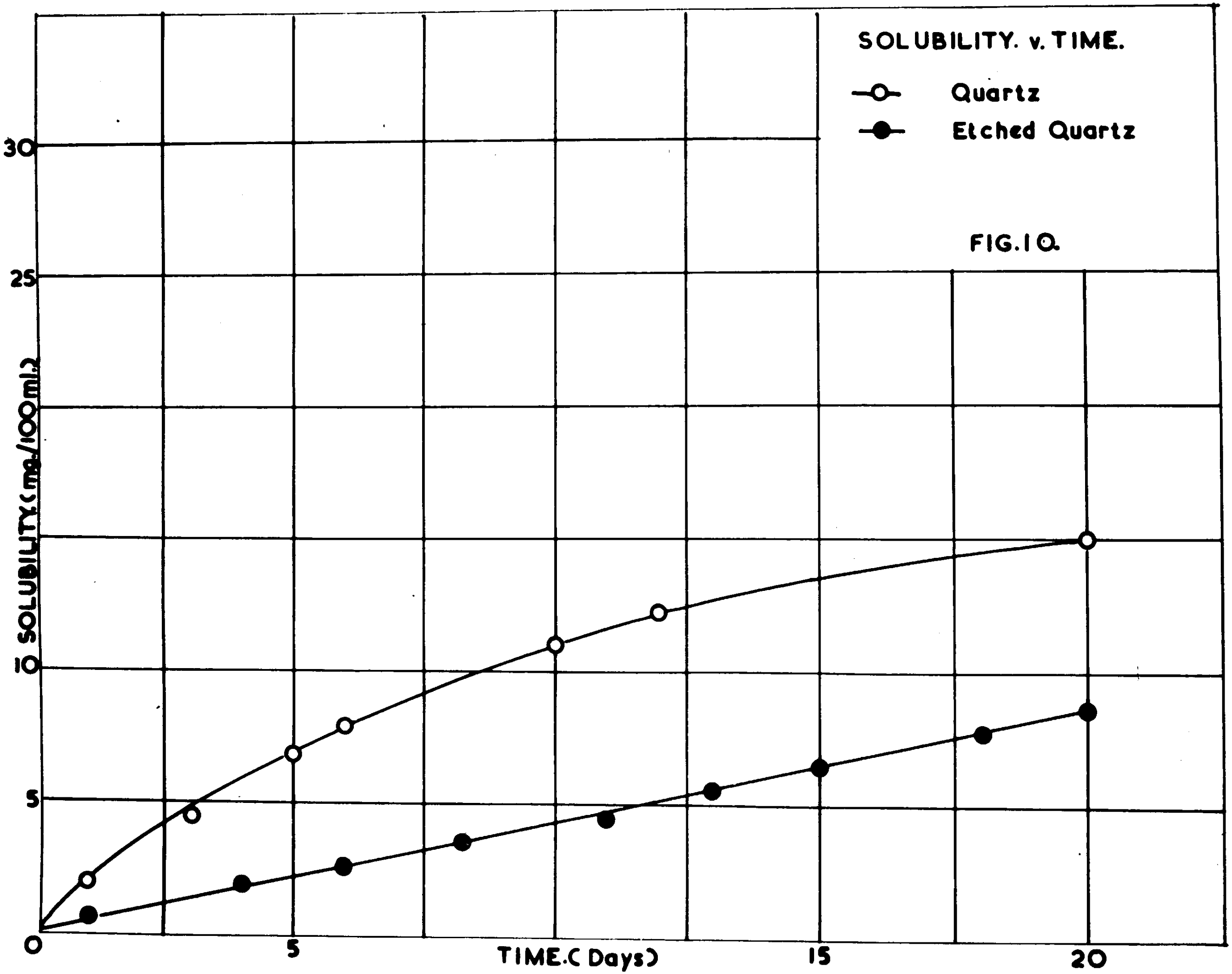

SOLUBILITY. v. TIME.
Quartz
Etched Quartz
SOLUBILITY (mg./100ml.)
0
5
10
25
30
TIME. (Days)
0
5
15
20

FIG.10.

of the rutile, it must either be very much thicker than that on quartz, or much thinner than detectable by these experiments.

(iii) (b) Solubility vs. Time for Pure Finely-ground Titanium Oxide.

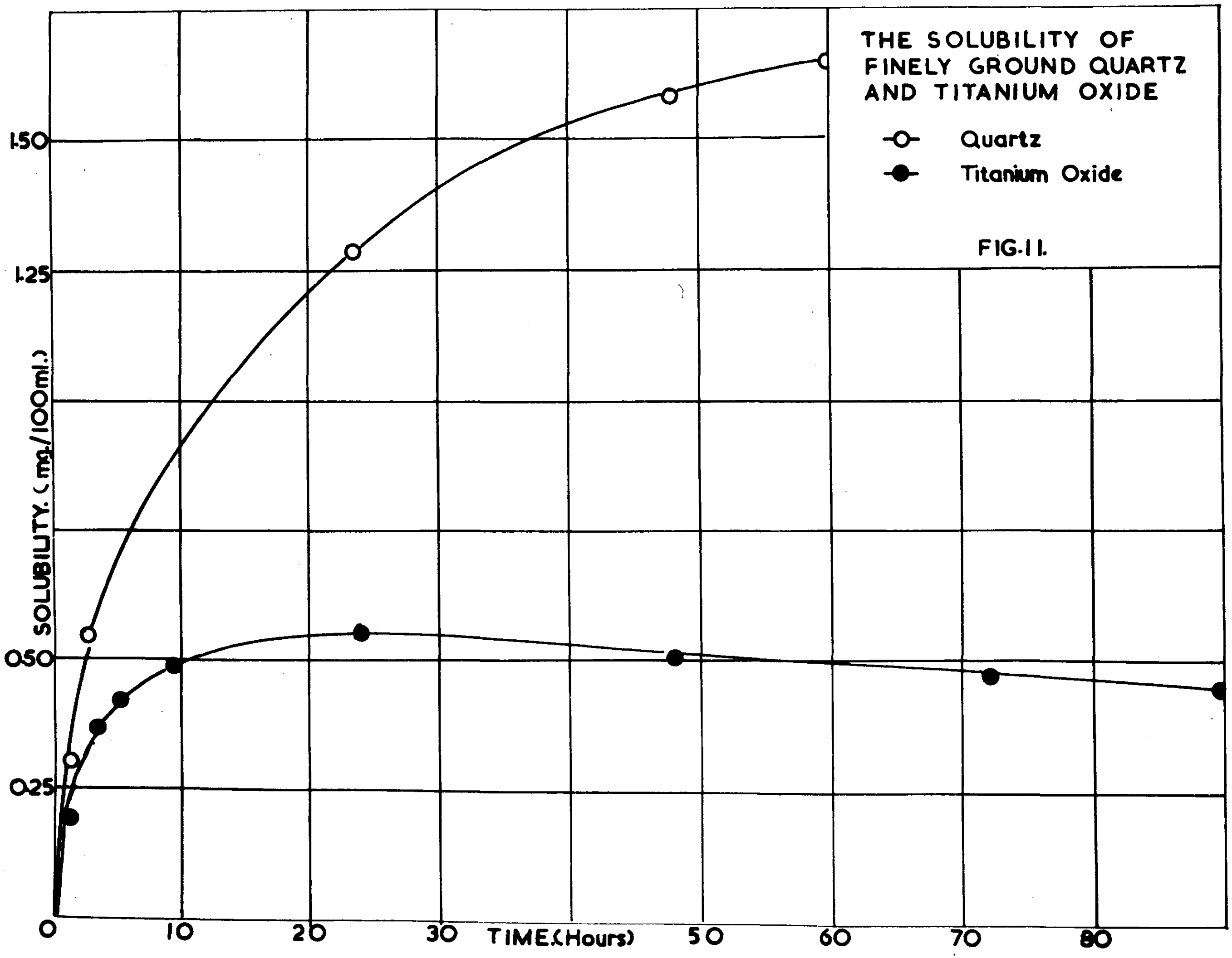
The TiO_2 dust T.1 was used, and the solvent was ca. 0.1N H_2SO_4 (pH 1.2). A mass-to-liquid ratio of 0.4 g. TiO_2/40 ml. 0.1N H_2SO_4 was used.

A series of tubes each containing 0.4 g. TiO_2 and 25 ml. 0.1N H_2SO_4 were continuously agitated in an air thermostat at 37°C. Tubes were removed at regular intervals, and the solvent filtered through a Whatman No.542 filter paper. The amount of titanium oxide in the solvent was then estimated.

A similar series of tests was carried out using a fine quartz dust with a borate buffer solvent (pH 7.5), the silica in solution being estimated by the molybdenum blue method.

The results of these tests are shown in Fig. 11. It is seen that the solubility of the quartz goes steadily towards a maximum value, whereas the titanium oxide solubility reaches a maximum value (at about 24 hours) and then decreases.

The experiment was repeated several times, and the results reproduced in every case, a decrease of about 20% of the peak value being obtained in the 66 hours after the highest value had been reached. This result may be explained (66) by the fact that a very fine powder exhibits a tendency to acquire a smaller surface (i.e. a larger particle size),



THE SOLUBILITY OF FINELY GROUND QUARTZ AND TITANIUM OXIDE

FIG.11.

the process being accomplished by the dissolution of the small-sized particles and their recrystallisation (from a solution which had achieved supersaturation) on the surface of the larger particles.

Alternatively, the undissolved solid may be regarded as a precipitate. When the solution attains some degree of supersaturation, further crystallisation will occur.

Over the 90 hours of the experiment, the quartz solutions had not reached saturation, and there was therefore no opportunity for this reprecipitation to occur.

4. Adsorption Experiments.

(a) (i) General.

To study adsorption by the dusts it was decided to use dyestuffs as the adsorbate since small amounts of these materials in solution can be readily estimated colorimetrically.

The results used for the adsorption of dyestuffs by siliceous dusts are taken from the work of Gibb (67).

(ii) Materials.

The rutile dusts used in this section of the work were R.2, R.2(A), and R.2(B). The average particle size of these dusts is 359 μ.

(iii) Investigation of the Types of Dye Adsorbed.

The method of investigating the adsorption of the different dyes was as follows:-

Solutions of different types of dyes were made up in water and diluted to give a reading on the most accurate portion of the EEL colorimeter scale, appropriate filters being used. 20 ml. of the dye solutions were added to Lusteroid tubes each containing 1 g. of dust R.2. The sealed tubes were continuously agitated for 1 hour, as were a series of tubes each containing 20 ml. of dye only. The intensity of the colours of the two sets of dye solutions (in and out of contact with the dust) were then estimated to determine whether adsorption had taken place.

The results of these qualitative tests are shown in Table IV. From the table it is seen that only basic dyes are adsorbed, and that this is also true for silica dust. Gibb (67) used Lochaline sand in his tests.

(iv) The Mechanism of Adsorption of Basic Dyes.

The basic dye methylene blue ionises in solution:-

$$C_{16}H_{18}N_3SCl \rightleftharpoons C_{16}H_{18}N_3S^+ + Cl^-$$

The colour of a basic dye is connected with the positively charged part of the molecule. This would seem to indicate that the adsorption is ionic, the dye being attracted to the dust surfaces by virtue of its positive charge in solution. Gibb (67) demonstrated that this was so, the particles of silica being negatively charged in aqueous suspension.

This experiment (which is similar to that described by Findlay (68) for demonstrating the electrophoresis of colloidal suspensoid sols) was

TABLE IV.

TYPE OF DYE	NAME OF DYE	Adsorption	
		Lochaline Sand	Rutile
Vat Dyes	Caledon Jade Green (XN300)	NIL	NIL
	Indigo	NIL	NIL
Direct Cotton Dyes	Chlorantine Fast Yellow (2RLL)	NIL	NIL
	Chlorazol Sky Blue (F.F.S.)	NIL	NIL
Acid Dyes	Solway Blue (PFN 125)	NIL	NIL
	Lissamine Fast Yellow (2G125)	NIL	NIL
Basic Dyes	Methylene Blue (2.BNS)	Adsorbed	Adsorbed
	Malachite Green (Ans. crystal)	Adsorbed	Adsorbed
	Methyl Violet (2B.200)	Adsorbed	Adsorbed
Sulphur Dyes	Sulphol Claret (RL.200)	NIL	NIL
	Sulphol Brilliant Green (10.G)	NIL	NIL

NOTE: All these dyes were of "Technical" quality.

repeated with titanium oxide as follows:-

A suspension of fine titanium oxide dust T.1. in water was made up. This suspension was placed in a U-tube which was fitted with copper electrodes, the suspension covering about 1/4" of the electrode. The tube was clamped in a position which was free from vibration and a direct current of 240 volts applied across the electrodes. After 30 minutes a migration of the dust particles was observed, the dust being repelled from the negative electrode. This shows that the titanium oxide dust is negatively charged in water suspension.

From these results it was concluded:-

1) Both silica and titanium oxide adsorb basic dyestuffs.
2) Silica and titanium oxide particles in water suspension are negatively charged.
3) The adsorption of basic dyes is due to ionic attraction of the positively charged dye ion by the oppositely charged surface.
4) Both silica and titanium oxide will adsorb other ionic materials which give rise to a positively charged ion in solution.

(b) The adsorption of Methylene Blue.

(i) The Purity of Methylene Blue. (tetramethylthionine chloride $C_{16}H_{18}N_3ClS.3H_2O$)

The dye used in the following quantitative tests was of B.P. quality. The British Pharacopoeia specifies its purity thus:-

As - Not more than 10 p.p.m.
Pb - Not more than 50 p.p.m.
Zn - This metal should be absent, and a

sensitive test is specified for it.

$C_{16}H_{18}N_3SCl$ - Not less than 80%.

The percentage of $C_{16}H_{18}N_3ClS$ in the dye used was estimated volumetrically by reducing an acid solution of the dye with standard titanous chloride solution and estimating the excess titanous chloride by titration with 0.1N ferric ammonium sulphate, using 10% ammonium thiocyanate solution as indicator. The whole estimation was carried out in an atmosphere of carbon dioxide. The Methylene Blue dye was found to contain 83% $C_{16}H_{18}N_3SCl$.

(ii) Calibration of the Colorimeter.

The Methylene Blue solution for the adsorption experiments was prepared by dissolving a weighed amount of the dye (3.1 mg.) in water and diluting to one litre.

This solution gave a suitable reading on the scale of the EEL colorimeter using a red filter Ilford No.608. From this solution 10 ml. quantities of known concentration were prepared (taking account of the fact that the purity of the dye was 83%) and these were used to calibrate the instrument. A straight line was obtained for the graph of colorimeter reading vs. dye concentration (mg./l.).

To obtain adsorption figures in g.-moles, the following calculation was made:-

From the calibration curve,

20 colorimeter divisions = 1.3 mg./l.

1 colorimeter division = 0.065 mg./l.

To reduce one litre by one colorimeter division requires the adsorption of 0.065 mg. of Methylene Blue.

To reduce 10 ml. by one colorimeter division requires the adsorption of 0.00065 mg. of Methylene Blue.

The molecular weight of Methylene Blue is 319.9.

$$\text{Now, } 0.00065 \text{ mg.} = 0.00000065 \text{ g.}$$

$$= \frac{0.00000065}{319.9} \text{ g.-moles}$$

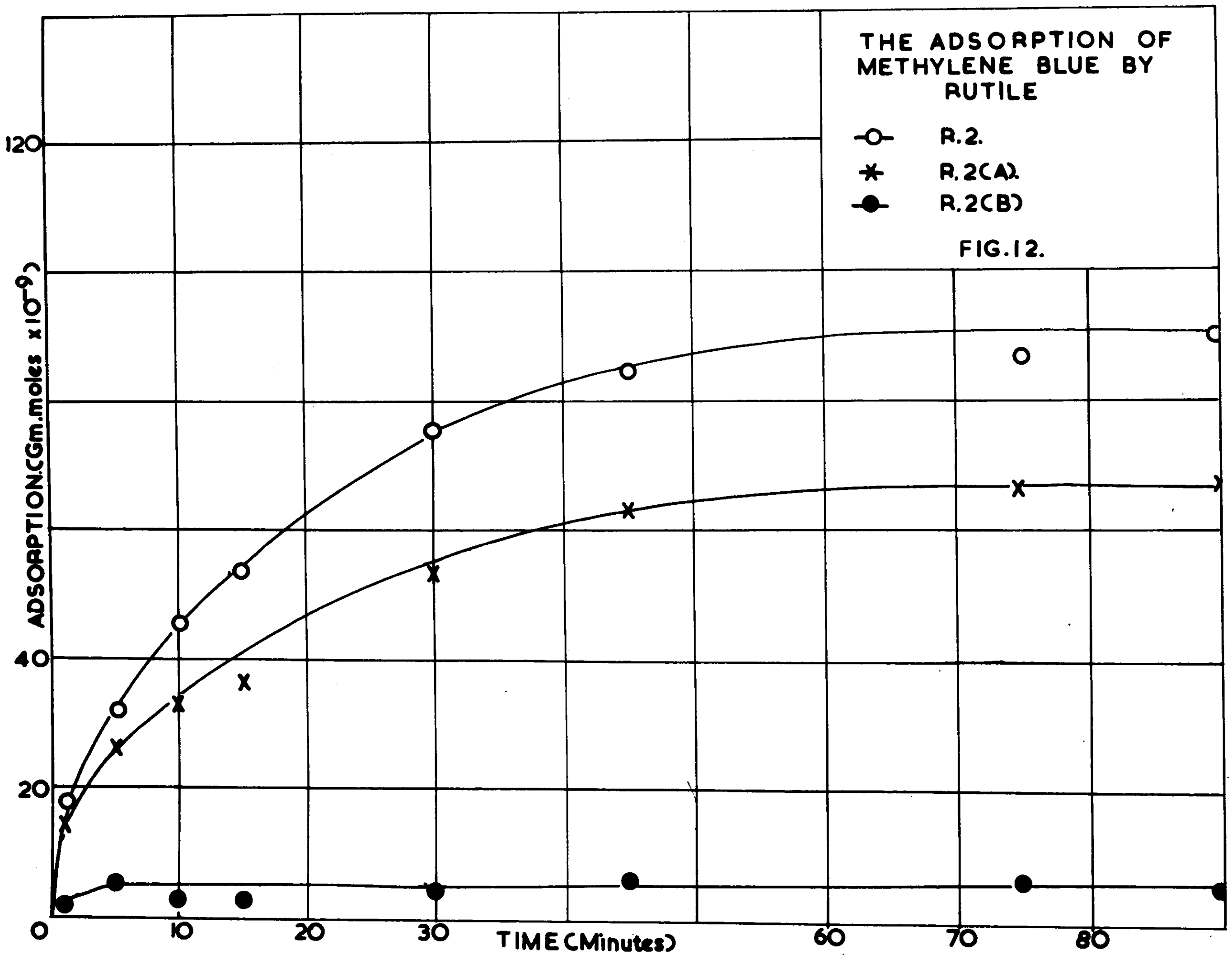
$$= 2.02 \times 10^{-9} \text{ g.-moles.}$$

To convert a fall in colorimeter reading due to adsorption to g.-moles of Methylene Blue adsorbed, it is therefore necessary to multiply the difference in readings before and after adsorption by 2.02×10^{-9}.

(iii) Adsorption Procedure.

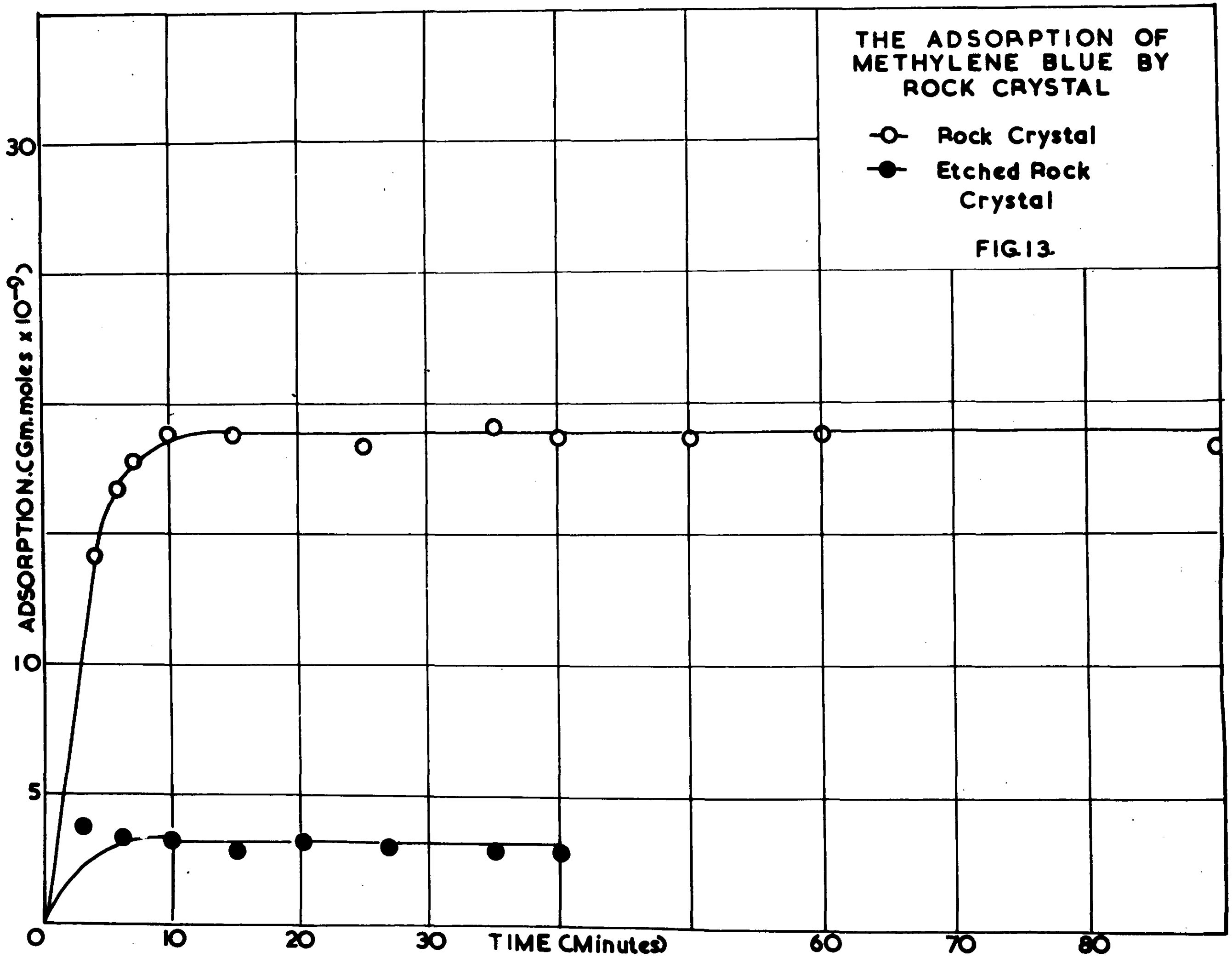
7 colorimeter tubes were carefully cleaned and dried. Two 1 g. lots each of R.2, R.2(A), and R.2(B) were weighed into the tubes, the empty one being required as a blank. A stop-clock was started, 10 ml. of dye solution run into each tube, and the tubes stoppered with waxed corks. At noted times readings were taken on the colorimeter for each tube until no further adsorption appeared to be taking place. The tubes were shaken regularly between the readings to ensure intimate mixing of the dust and the solution.

The results of these tests are shown in Fig. 12. Fig. 13 shows



THE ADSORPTION OF METHYLENE BLUE BY RUTILE

FIG.12.



THE ADSORPTION OF METHYLENE BLUE BY ROCK CRYSTAL

FIG.13.

the adsorption of Methylene Blue by quartz dust with and without the "high-solubility" layer.

From these figures it can be seen that, over a period of 90 minutes, untreated rutile adsorbs four times as much dye as quartz, and hydrochloric-acid-treated dust adsorbs three times as much dye as quartz.

These results are compared on a weight basis. The average particle size of the rutile dusts is greater than that of the quartz dust used by Gibb (67). Their specific surface, therefore, is less, and adsorption figures compared on a specific surface basis would show an even greater difference.

The adsorption of Methylene Blue by the hydrofluoric-acid-treated dusts is very small. This is said to be due, in the case of quartz, to the removal of an amorphous surface layer. It could also be due, as suggested by Gibb (67), to repulsion of the positively charged dye ions by hydrogen ions adsorbed on the surface of the dust, and this is probably the reason for the slight adsorption of Methylene Blue by dust R.2(B).

The maximum adsorption for quartz (19×10^{-9} g.-moles) is reached after 10 minutes, while that for rutile (90×10^{-9} g.-moles) is not reached until the dust and the dye have been in contact for about one hour.

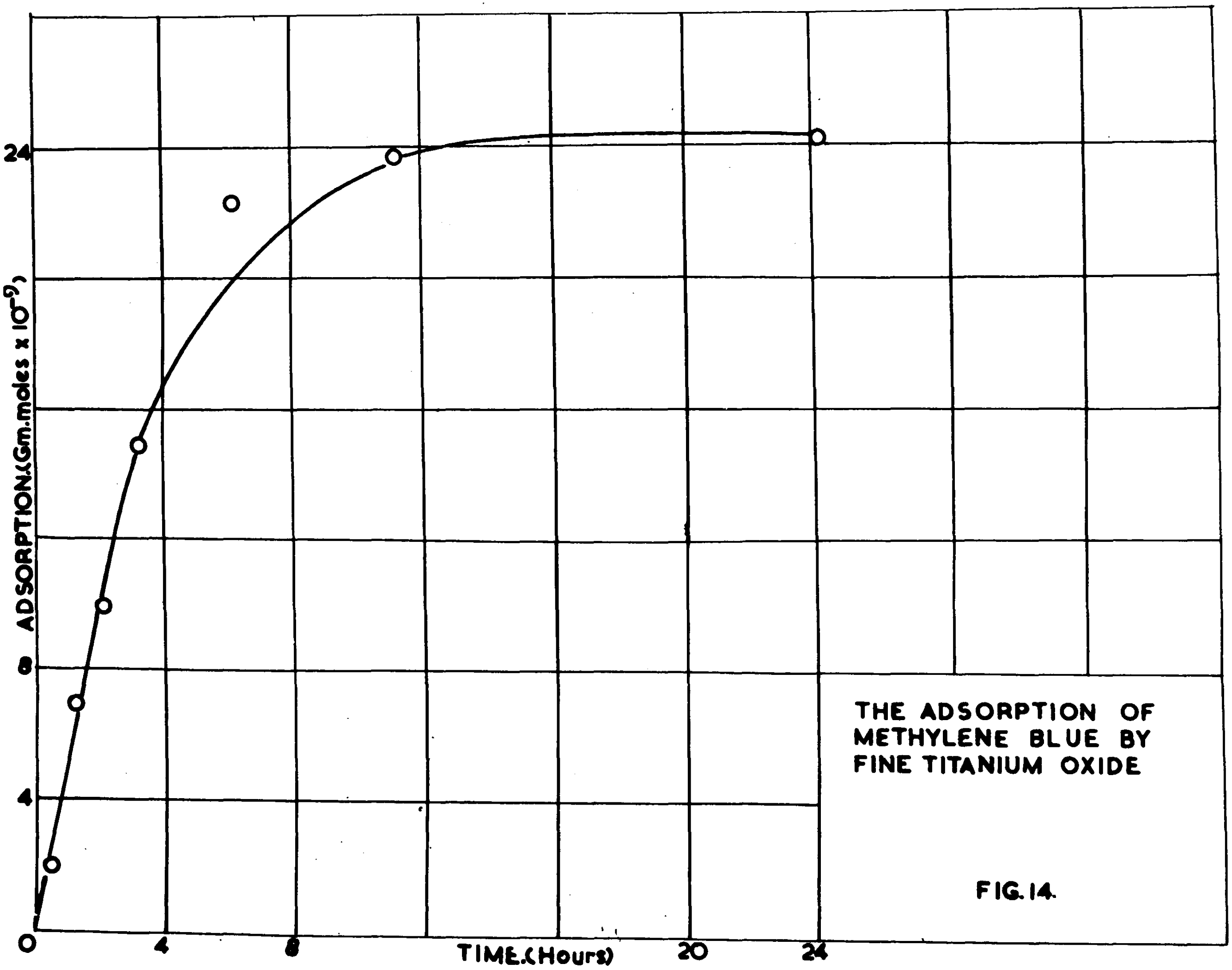
(iv) The adsorption of Methylene Blue by Fine Titanium Oxide.

The adsorption of Methylene Blue by rutile may be due to the iron oxides and silicates present. It was decided, therefore, to investigate this by examining the adsorption of the dye by pure titanium oxide. This was only available in the form of the very fine amorphous dust T.1 which did not settle out from a suspension in dye solution under gravity. The adsorption procedure was accordingly modified:-

Titanium oxide (0.25 g.) was weighed out into several clean, dry colorimeter tubes. A stop-clock was started, 10 ml. of Methylene Blue solution (3.1 mg./l.) run into each tube, and the tubes sealed with waxed corks. The tubes were shaken regularly to ensure an even suspension of the dust in the dye solution. To determine the adsorption at any time, a small quantity of aluminium sulphate (A.R.) was added to a tube which was then centrifuged for 15 minutes at 3000 r.p.m. (Centrifuging alone did not break down the suspension completely, and the aluminium sulphate was required as a coagulant.) The liquid was then transferred to a clean colorimeter tube and compared with 10 ml. of the original dye solution to which aluminium sulphate had been added. An EEL colorimeter with a red filter (Ilford No.608) was used as previously.

The adsorption was measured at regular intervals, the time being taken as the time at the start of the centrifuging. The results are shown in Fig. 14.

These results show that Methylene Blue is adsorbed by finely ground titanium oxide to the extent of 24×10^{-9} g.-moles in 24 hours, and that the adsorption figures obtained using the natural dusts R.2, R.2(A), and



THE ADSORPTION OF METHYLENE BLUE BY FINE TITANIUM OXIDE

FIG. 14.

R.2(B), although they may be modified by impurities, are not altogether due to them, i.e. titanium oxide does, in itself, adsorb basic dyestuffs to a considerable extent.

(c) The Adsorption of Malachite Green.

Rutile adsorbs much more Methylene Blue than does quartz, and it was decided to repeat the adsorption experiments using Malachite Green, a basic dye of the triphenylmethane type, to see if this much greater adsorption was again obtained.

(i) Estimation of the Purity of the Malachite Green.

The dye used was of technical quality. The purity of the material was found by titration of a solution of the dye at boiling point with standard titanous chloride solution in presence of Rochelle salt in an atmosphere of carbon dioxide. The end point is reached when the colour of the dye remains destroyed for more than 3 minutes. By this method the purity of the dye was found to be 88%.

(ii) Calibration of the Colorimeter.

The EEL colorimeter was calibrated against known solutions of the adsorbate as in the Methylene Blue experiments. A red filter (Ilford No.205) was used for this dye.

The calibration graph was a curve, not a straight line. Differences in colorimeter readings could not, therefore, be directly converted to adsorption in g.-moles. The concentration of dye in the solution corresponding to the colorimeter reading for the tube with no dust was obtained from the calibration curve, as was the concentration of the dye in the tubes containing dust. The difference in these is the adsorption in mg. dye from one litre of solution. From this the adsorption from 10 ml. was calculated, and the adsorption in g.-moles obtained by dividing the adsorption in grams by the molecular weight of the dyestuff (350.5).

(iii) Adsorption Procedure.

The adsorption procedure was the same as that for Methylene Blue. The dusts R.2, R.2(A), and R.2(B) were used.

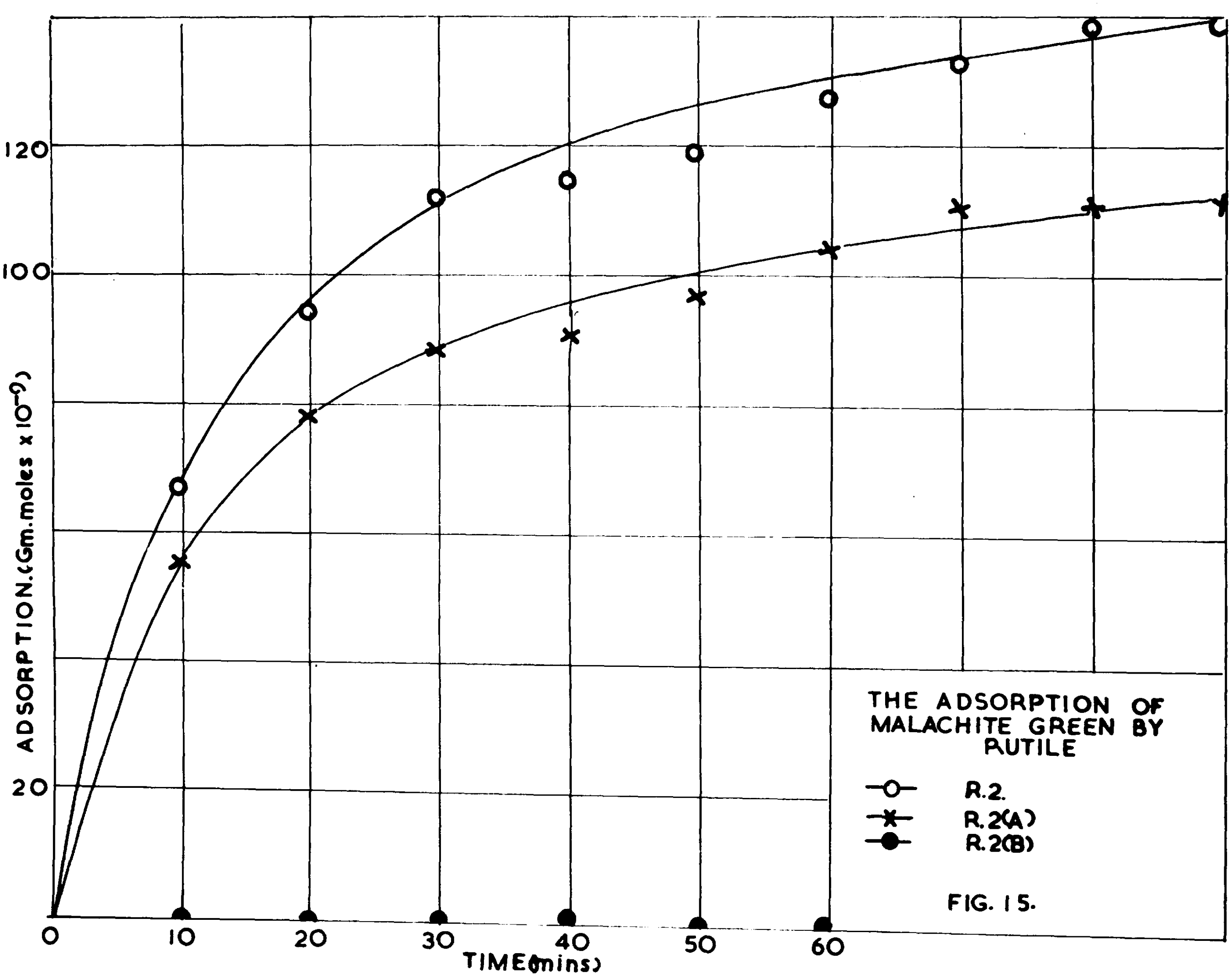
The results are shown in Fig. 15. The results for the adsorption of Malachite Green by quartz are shown in Fig. 16, and are taken from the work of Gibb (67). No measureable adsorption was obtained for Malachite Green on etched quartz.

Again, more dye is adsorbed by rutile than quartz - twice as much in this case. Over a period of 90 minutes rutile adsorbed 140 x 10^{-9} g.-moles of Malachite Green and did not appear to have reached the maximum, while over the same period quartz had adsorbed 70 x 10^{-9} g.-moles (a steady value).

5. General Discussion of Results.

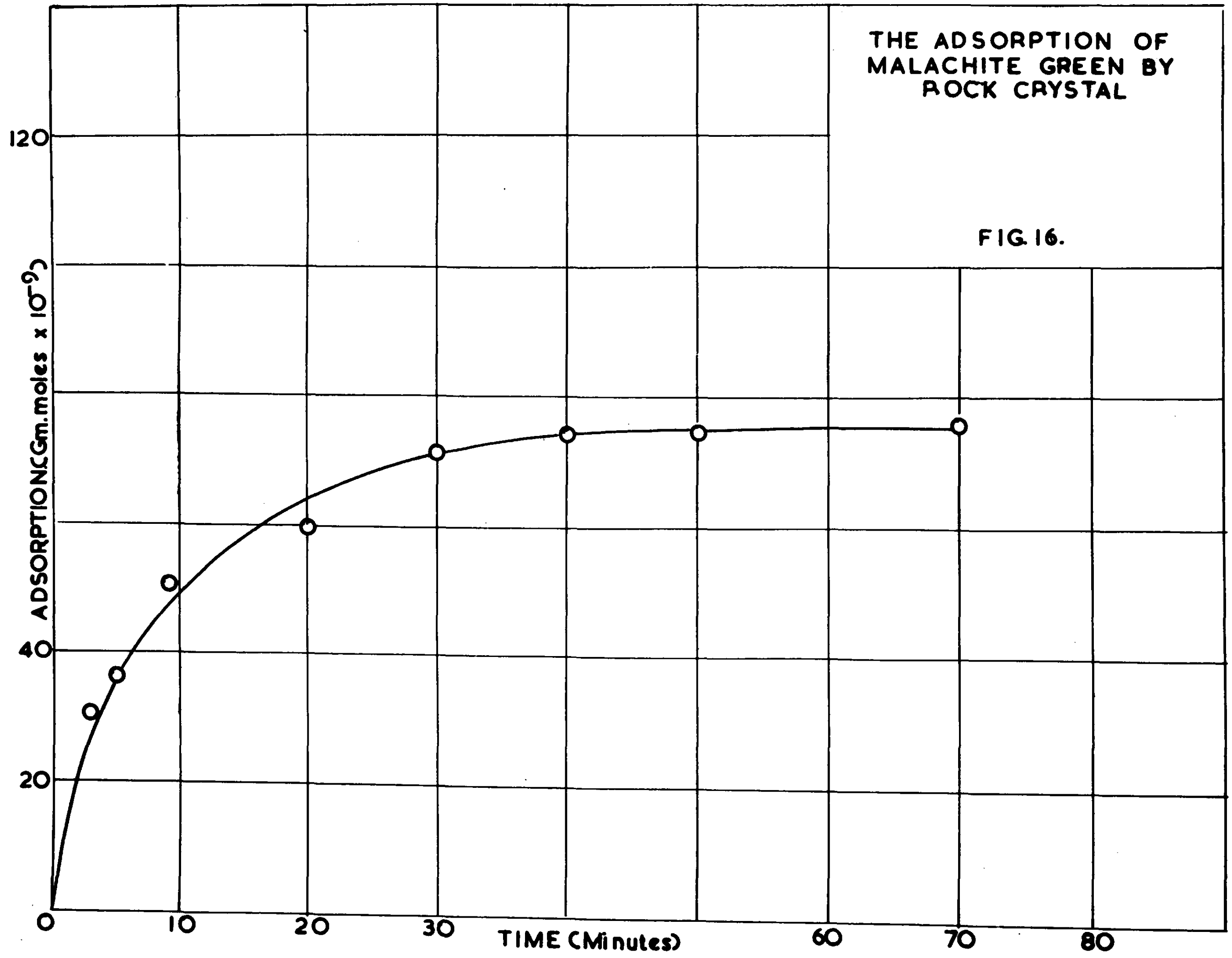
(i) Solubility *vs.* pH.

The graphs of solubility *vs.* pH for rutile and quartz are similar in shape. At pH 7.5, the pH of the lung fluids, the solutility of rutile is too small to be detected by the analytical methods available.



THE ADSORPTION OF MALACHITE GREEN BY RUTILE

FIG. 15.



THE ADSORPTION OF MALACHITE GREEN BY ROCK CRYSTAL

FIG. 16.

Quartz had a solubility of the order of 1 mg./100 ml. under the same conditions. This shows that the solubility of titanium oxide dust in lung fluids is negligible. If a solution of titanium oxide in the lungs is fibrogenic, it would probably take longer than the average working life for the concentration to reach dangerous proportions in the lungs.

(ii) The existence of a "High-Solubility Layer" on Rutile.

The solubility tests carried out give no indication of the existence of such a layer on rutile. The fact that treatment of the dusts with hydrofluoric acid results in a considerable decrease in the adsorption of basic dyestuffs by both quartz and rutile, which treatment is known to remove the "high-solubility layer" from quartz, is not evidence of the existence of such a layer on rutile, since etching with hydrofluoric acid increases the solubility of rutile. The decrease in adsorption of basic dyes is probably due to adsorption of hydrogen ions from the acid by the dust resulting in a decrease in the negative charge on the surface (67).

If such a "high-solubility layer" exists on the surface of the titanium oxide dusts, it must be either so thick or so thin that it has not been detected by the solubility experiments. In other words, there is no experimental evidence for its existence.

(iii) Adsorption of Dyestuffs.

The results of the adsorption experiments show that rutile and quartz adsorb the same type of dyestuffs, namely, the basic dyes which ionise in solution to give a positively charged colour-ion. It may be inferred that other materials which behave similarly in solution will also be adsorbed by quartz and rutile.

(iv) General.

Rutile has negligible solubility at the pH of the lung fluids and at body temperature. It adsorbs to a greater extent similar types of material to quartz. Since rutile is a pathogenically inert material, it would appear that adsorption plays, at most, a small part in the mechanism of silicosis.

This work has not, however, taken into account the possibility that there may be some preferential adsorption of certain materials from the lung fluids by quartz, which does not occur with rutile. This type of adsorption may play some part in the mechanism of the production of silicosis.

SECTION 3.

The Preparation of Synthetic Quartz.

Introduction.

Much work has been done on the solubility and pathogenicity of naturally occurring siliceous dusts in relation to the pneumoconiosis problem. The effect of small quantities of impurities, which seem always to be present in natural materials, is not readily determinable owing to their very nature. That they may be of importance is instanced by "aluminium therapy", in which the inhalation of small quantities of finely ground aluminium metal or alumina considerably reduces the solubility and fibrogenicity of siliceous dust in the lungs.

A detailed examination of the effect of trace quantities of impurities on the solubility and fibrogenicity of siliceous dusts is therefore of interest in this problem.

The impurities can occur in two ways:-

(a) As a physical mixture with the silica (i.e., a polyphase system).

(b) Occupying some place in the structure of the silica crystal lattice (i.e., a single-phase system).

Type (a) can readily be investigated by the preparation of a series of mixtures of natural quartz (purified by acid-extraction, washing, etc.) or commercial amorphous silica with Analar reagents representing the natural impurities.

The investigation of type (b) requires a method of synthesising quartz such that experimental impurities are negligible (and what constitutes "negligible" in this problem is not really known). Also, to avoid the necessity for much crushing and grinding, and the introduction of further accidental impurities by these operations, the crystals produced should be small (say 90 mesh B.S., with an upper limit of 0.5 mm.). Further, it must be possible to produce successive batches of crystals with identical physical and chemical properties.

Impurities in the lattice can be visualised as existing in several ways:-

(i) by substitution for a silicon atom in the crystal lattice;
(ii) by occupying a normal space in the regular lattice;
(iii) by occupying a flaw in the defective lattice.

Again, deposition of the impurities may be regular, random, or periodic. The crystal lattice may be strained and altered in different degrees by any combination of these factors, and the solubility and other properties (e.g. adsorptive capacity) altered.

The aim of this section of the work was to develop a method of synthesis of quartz which could be used to study the factors discussed above.

Review of Methods for Synthesis of Quartz.

The use of quartz for oscillator crystals in high-frequency transmitters, and the dearth of suitable natural crystals during the war, led to much research into the growing of synthetic quartz.

Attempts have been made for over a century to grow synthetic quartz. Experiments such as those of Schafhaütl (69), who heated freshly precipitated silica in Papin's digester, and de Sénarment (70, 71), who added "mineralisers" such as hydrochloric acid in an attempt to improve the quality of the product, lasted for many days, some even for several months, and resulted in the production of small quantities of microscopic quartz crystals.

Spezia (72, 73) showed that large crystals could be grown in a few months provided that an adequate source of raw material was available. His method was based on the fact that quartz is more soluble in a solution of sodium metasilicate at temperatures above 300°C. than below it. He placed a silver-wire basket containing quartz chips in the hot part of an autoclave (which was heated at the top by gas and cooled by water at the bottom) and a truncated quartz crystal in the cool section. The solution containing dissolved silica flowed down past the quartz crystal, became supersaturated at the lower temperature, and silica separated out as quartz on the crystal.

The modern methods for the synthesis of quartz for oscillator crystals have been developed from Spezia's method. It was decided to adapt one of these modern methods, the isothermal method, to the requirements of this work.

The Isothermal Synthesis of Quartz.

This method was developed in this country by the Woosters *et al.* (74) and independently by Nacken (75) in Germany.

In this method, a uniform temperature is used, in place of Spezia's temperature difference, the growth cycle being dependent on the much higher solubility of silica in the vitreous than in the crystalline form. Silica glass is used to replenish the silica content of the sodium metasilicate solution as silica is deposited on the seed crystal.

The growth is carried out in an autoclave capable of withstanding pressures of the order of 1,000 atmospheres at a temperature of 360°C. The solution used contains sodium metasilicate (usually 10% sodium metasilicate W/V) and a mineralizing substance, commonly potassium acid fluoride, whose function is to improve the crystalline perfection of the deposited quartz.

The source material, transparent Vitreosil rod (76) (the translucent grade is unsuitable because it devitrifies very rapidly), is suspended above the seed plate. The Vitreosil rod and the seed crystal are suspended in the autoclave by a silver wire. The volume of the liquid used is that volume which is calculated to give the required pressure at the working temperature (usually 360°C.). The growth cycle is normally of eighteen hours duration.

Adaptation of the Method.

Autoclave No. 1.

The first autoclave used in this work was made of high-tensile steel (77). It had a nominal internal volume of 100 ml., and a bore of 184 mm. A mild-steel lens ring gave a complete seal for pressures of the order of 1,000 atmospheres at 360°C. The seatings on the body and lid of the autoclave were ground to conical surfaces so that a line seal was formed with the spherically ground surfaces of the lens ring.

Since large crystals are not required, it was decided to dispense with the seed crystal and replace it with a silver gauze. The quartz form of silica being less soluble than the amorphous, it was expected that the silica would deposit out on the gauze as quartz.

Transparent Vitreosil rod was used as the source material, a portion 40 mm. long x 10 mm. in diameter being used in each 12 hour run.

The solvent used was a 10% solution of sodium metasilicate. The volume of the solution required to give a pressure of 1,000 atmospheres at 360°C. (the working temperature) is calculated from the formula

$$\frac{\text{Available Volume}}{\text{Volume of liquid required}} = 1.3$$

where "available volume" = volume of autoclave - volume of its solid contents (gauze + wire + source).

The autoclave was heated in an electric furnace, the temperature of which was thermostatically controlled to 360° ±5°C. At the end of a run the autoclave was allowed to cool naturally from 360°C. to 150°C. It was then quenched by immersion in cold water.

The method of suspending the source rod was simply to file a notch in it and tie it by a piece of silver wire below the silver gauze. The silver gauze was in turn suspended by a silver wire to a hook in the lens ring. This method was not satisfactory, since no matter how firmly the glass was tied its size decreased during the run, and some part of the rod fell to the bottom of the autoclave. It was found much simpler and more effective to make a "parcel" of the rod with the gauze and suspend the parcel inside the autoclave.

Discussion.

The runs carried out using this autoclave were not satisfactory. Very little material was obtained from the first few runs, most of the silica depositing on the walls of the vessel. The silica which was recovered from the gauze was discoloured (yellow). The deposit on the walls grew rapidly, and a great deal of material accumulated in the bottom of the autoclave. Because of the narrow bore it was very difficult to remove the adherent material. This could only be done by heating the inside of the tube with an air-gas blowlamp; because of the different coefficients of expansion of the quartz and the steel, the quartz then cracked away from the sides of the vessel.

The high temperatures involved in this procedure cause conversion of the quartz to the various different forms (α, β, γ) reversion from which, on cooling, is never complete. Further, the quartz is liable to contamination by the gases (CO, CO_2, hydrocarbons, etc.) and by metallic products from the walls of the autoclave.

After such violent treatment the quartz was, of course, of no use for the solubility tests.

After the autoclave had been cleaned in this fashion, and with hydrofluoric acid, it was silver plated in an attempt to prevent attack on the steel walls by the metasilicate solution and subsequent iron contamination of the product. At the same time the "parcel" method of suspending the Vitreosil rod was adopted.

The silver-plating proved successful in eliminating contamination for several runs, and some white, opaque material was obtained from the silver gauze at the end of each run.

Examination of this material under the microscope showed many quartz-like crystals. X-ray examination confirmed that the material was quartz.

From each of five runs an average of 1 g. of material was obtained. Since the source-rod weighs approximately 8 g., this represents a yield of only 12.5%. The remainder of the silica deposited out on the walls of the autoclave.

After five runs a considerable deposit of quartz had built up on the walls of the autoclave. There were also gaps where the plating had broken away as a result of abrasion by the gauze and the temperature changes to which the autoclave was subjected.

It was decided to design and make another autoclave in an attempt to overcome the difficulties experienced with the first one.

Autoclave No. 2.

After consideration of the materials available it was decided that the second autoclave should be made of stainless steel. It was thought that stainless steel would be resistant to attack by sodium metasilicate solution under the conditions of the runs, while its physical properties were such as to give the required strength without undue bulk. It was also decided that for general ease of working the autoclave should be capable of being opened at both ends.

The autoclave was designed and made in "Staybrite" F.D.P. stainless steel. (A drawing is attached to the inside back cover.) The studs were of high-tensile steel.

The working conditions were initially the same as for autoclave No. 1, i.e. 1,000 atmospheres pressure at 360°C. using a 10% sodium metasilicate solution and a transparent Vitreosil rod, 40 mm. long x 10 mm. diameter, as source, the rod being wrapped in a silver gauze.

Discussion.

It was considered that the use of stainless steel would avoid the corrosion and contamination problems encountered with the first autoclave. This did not prove to be the case. The product from the first run carried out in this autoclave was also yellow and discoloured. It is not possible to silver-plate stainless steel because of the oxide film present on the surface. The autoclave was, however, chromium-plated in an attempt to cut down contamination by corrosion. In addition some other solutions were tried as solvents.

Details of some of the runs carried out are given in Table V, from which the following conclusions may be drawn:-

(1) Since the effect of the method of quenching is so marked, it appears that the mechanism of the production of quartz is different from that occurring in the isothermal process for the production of oscillator crystals. In the absence of a quartz crystal seed it seems that very little deposition occurs until the autoclave is quenched, when the dissolved silica is deposited in the least soluble form (quartz) from the now supersaturated solution.

(2) The combination of sodium oleate as corrosion inhibitor, and a protective coating of silica on the walls, appears to be efficient in preventing contamination of the products. Very little silica deposited out on the upper lens ring, and this left a chromium-iron surface exposed to the sodium metasilicate solution.

It seems to be necessary, therefore, before crystals can successfully be grown free of impurity, that a few runs should be carried out to allow the formation of a thin wall of quartz inside the autoclave.

(3) As a result of (1) above, the duration of the run need only be

such as to allow complete dissolution of the Vitreosil rod.

Plates 10 and 11 show the silver gauze and the transparent Vitreosil rod before and after the run. The rod has been completely dissolved, and deposited silica can be seen on the gauze.

Plates 12, 13, and 14 show Vitreosil source material crushed to the size of the product and the products as seen under a microscope. In the latter plates definite crystals of quartz can be seen.

Solubility Tests.

Solubility tests were carried out on some of the synthetic quartz. The results are shown in Table VI. The dusts were all boiled in distilled water to remove sodium metasilicate solution, and dried at 120°C. for 90 minutes.

TABLE V.

SOURCE	LIQUID PHASE	DURATION OF RUN	NOTES
40 mm. long x 10 mm. diameter transparent Vitreosil rod (8.25 g.) wrapped in silver gauze.	10% sodium metasilicate solution.	12 hours	No crystals on gauze. Weight of rod 4.73 g. i.e. <u>ca.</u> 3.5 g. silica removed from rod and either deposited on walls or retained in solution. No change in volume of metasilicate solution i.e. no leaks but solution discoloured (yellow). Try longer run.
As above Rod weight 8.0 g.	As above	16 hours	Traces of crystals lightly attached to walls and to suspending silver wire. A few crystals on gauze. Most of the silica removed from the source deposited in bottom lens ring.
As above	As above	16 hours	The quartz crystals from previous run were left on the gauze and walls to provide seeds for deposition during this run. Again

SOURCE	LIQUID PHASE	DURATION OF RUN	NOTES
			only slight attack on source. The residue wrapped in the gauze consisted of a core of unchanged Vitreosil with a covering of discoloured yellow material. The water used in making up the sodium metasilicate solution was distilled from an iron still. May be cause of contamination.
40 mm. long x 10 mm. diameter transparent Vitreosil rod wrapped in wire gauze. Rod weight 7.53 g.	10% solution of sodium metasilicate in water distilled from a glass still (66.9 ml.).	16 hours	Some crystals obtained from gauze and from walls of autoclave, but some discoloured yellow. 1.28 g. of source material remained unattacked. Yield should therefore be approximately 6 g. Yield is 1.5 g. i.e. 25%.
As above Rod weight 7.5 g.	As above	16 hours	The sodium metasilicate used was tested and shown to be free from iron. Walls of autoclave now appear to have a thin layer of

SOURCE	LIQUID PHASE	DURATION OF RUN	NOTES
			deposited material. Some crystals obtained, but still discoloured and still only small quantity. 0.70 g. of source material recovered.
As above	As above	16 hours	All source material used up. Yield still unsatisfactory and still discoloured. Stainless steel evidently does not resist attack by sodium metasilicate solution under these extreme conditions of temperature and pressure.
As above	As above	16 hours	First run after chromium-plating of autoclave Some attack of source material, but no crystals obtained.
Unused materialfrom previous runs to weight approx. 8 g.	10% sodium metasilicate soln. Liquid from previous run	16 hours	If the silica dissolved from the source is being retained in solution and not deposited out the re-use of an old solution should remedy this. Source material not completely dissolved. A

SOURCE	LIQUID PHASE	DURATION OF RUN	NOTES
	made up to 66.9 ml. and re-used (only 2 ml. fresh soln. required).		few crystals were obtained. A green line appeared on the walls of the autoclave - possibly chromium salts. The sodium meta-silicate solution was strongly coloured yellow. Analysis showed Fe traces but no Cr.
40 mm. long x 10 mm. diameter transparent Vitreosil rod.	5% Sodium carbonate solution (66.9 ml.)	16 hours	If contamination is due to attack on plating, attack by sodium carbonate solution would be expected to be greater. Product a mass of white gelatinous material. Solution too strongly alkaline. No visible sign of contamination. Source only partly used up.
Unused Vitreosil rod from previous runs to weight approx. 8 g.	0.03N Sodium carbonate soln. (0.16 g./100 ml.) (66.9 ml.)	16 hours	Negligible attack of source. No dis-colouration. Note deposition occurring on walls at base of autoclave, away from source. Try separating source and gauze.

SOURCE	LIQUID PHASE	DURATION OF RUN	NOTES
40 mm. long x 10 mm. diameter transparent Vitreosil rod contained in a basket of silver gauze lying in base of autoclave - well separated from gauze on which deposition was intended to occur.	0.03N Sodium carbonate solution (0.16 g./100 ml.) (66.9 ml.)	60 hours	Few crystals obtained. No signs of discolouration of either crystals or solution. (Little attack on source material.) Try stronger sodium carbonate solution.
Transparent Vitreosil rod residue from previous run. Weight to approx. 8 g. Rod supported in base of autoclave as in	0.3N Sodium carbonate soln. (1.6 g./100 ml.) (66.9 ml.)	24 hours	Approx. half of source rod dissolved. Negligible quantity of crystals on gauze. Some on gauze supporting rod in base of autoclave. Walls of autoclave now appear to have coating of deposited silica.

SOURCE	LIQUID PHASE	DURATION OF RUN	NOTES
previous run.			
40 mm. long x 10 mm. diameter transparent Vitreosil rod. Supported in base of autoclave as previously.	*ca.* 0.6N Sodium carbonate soln. (3.0 g./100 ml.) (66.9 ml.)	24 hours	Considerable dissolution of source material. Solution milky. Few crystals on upper gauze. The silver gauze supporting the rod had considerable deposit of silica. Also some deposition on bottom of autoclave. Solution too alkaline. Try using only one gauze.
40 mm. long x 10 mm. diameter transparent Vitreosil rod. Allowed to lie unsupported in base of autoclave.	*ca.* 0.4N sodium carbonate soln. (2.0 g./100 ml.) (66.9 ml.)	60 hours	No crystals on gauze. Solution clear. About half of source dissolved. Autoclave now has silica lining about 1/16" thick at base thinning down to fine skin at top. Having source and gauze separate does not appear to be satisfactory. Revert to "parcel" method. Very long duration of run does not appear to be necessary.

SOURCE	LIQUID PHASE	DURATION OF RUN	NOTES
40 mm. long x 10 mm. diameter transparent Vitreosil rod, wrapped in silver gauze and suspended from top of autoclave as in original experiments.	10% Sodium metasilicate soln. (66.9 ml.)	24 hours	Source completely dissolved. Most of deposition in base of autoclave. Some green-tinged crystals on gauze. Solution discoloured yellow.
As above	10% Sodium oleate solution (66.9 ml.)	24 hours	No attack on source. No crystals, no contamination.
As above	10% Sodium metasilicate soln. (66.9 ml.) + 0.1 g. sodium oleate (as inhibitor).	24 hours	Sodium oleate is common corrosion inhibitor. All source material gone. Very few crystals on gauze, but solid mass of deposited silica in bottom lens ring, which material was white and free from visible impurity. Try altering method of quenching to prevent base being cooled more rapidly than top.

SOURCE	LIQUID PHASE	DURATION OF RUN	NOTES
40 mm. long x 10 mm. diameter transparent Vitreosil rod.	10% Sodium meta-silicate soln. (66.9 ml.) + 0.1 g. sodium oleate.	24 hours	Autoclave quenched by running cold water on top thus cooling top before base. Vitreosil completely dissolved. 50% yield of material on gauze. Visibly pure. (i.e. no discolouration visible to eye.) Material from gauze boiled for 5 min. to remove adherent solution. Dried 90 min. at 120°C. X-ray analysis showed 78 ±5% quartz (as distinct from amorphous) Fe and Cr absent by analysis (78).
40 mm. long x 10 mm. diameter transparent Vitreosil rod wrapped in gauze as previously with second gauze suspended below to	10% Sodium meta-silicate soln. (66.0 ml.) + 0.1 g. sodium oleate.	24 hours	Yield 3.5 (44%) of good appearance. After washing and drying as previously, X-ray analysis showed 84 ±5% quartz (78).

SOURCE	LIQUID PHASE	DURATION OF RUN	NOTES
increase useful area for deposition.			
40 mm. long x 10 mm. diameter transparent Vitreosil rod + 0.04 g. Aluminium powder suspended in solvent. Only one gauze.	10% Sodium metasilicate soln. (66.9 ml.) + 0.1 g. sodium oleate.	24 hours	Yield 3.2 g. (40%).

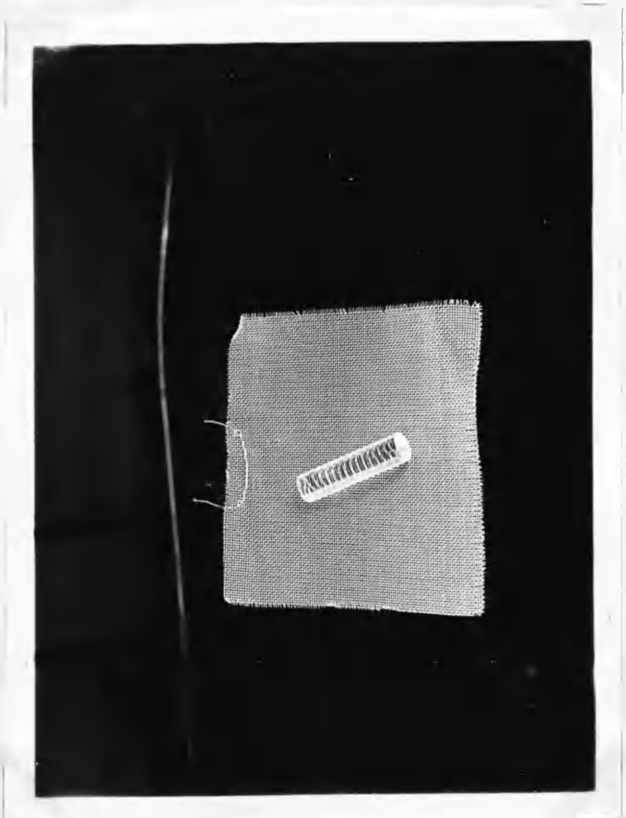


PLATE 10.

Silver gauze and transparent Vitreosil rod source before quartz synthesis run.

PLATE 11.

Silver gauze and adherent product after quartz synthesis run.

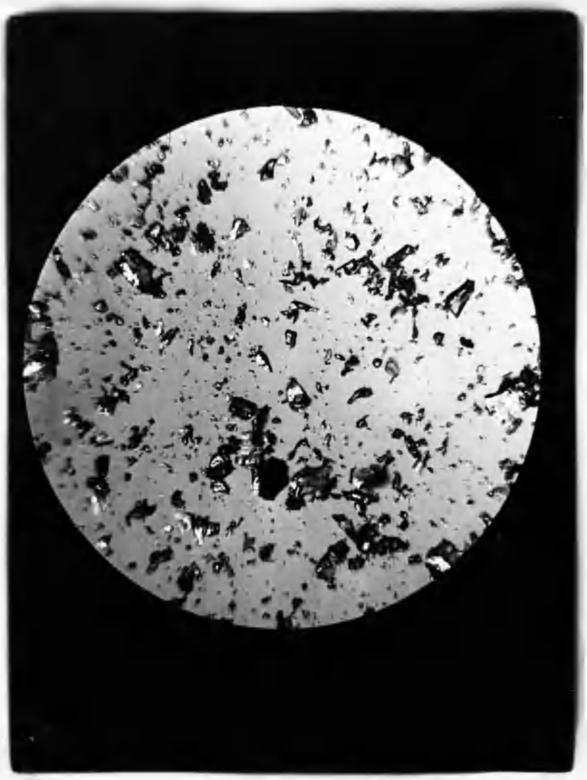


PLATE 12.

Vitreosil source crushed to same size as product. (Magnification x 10)

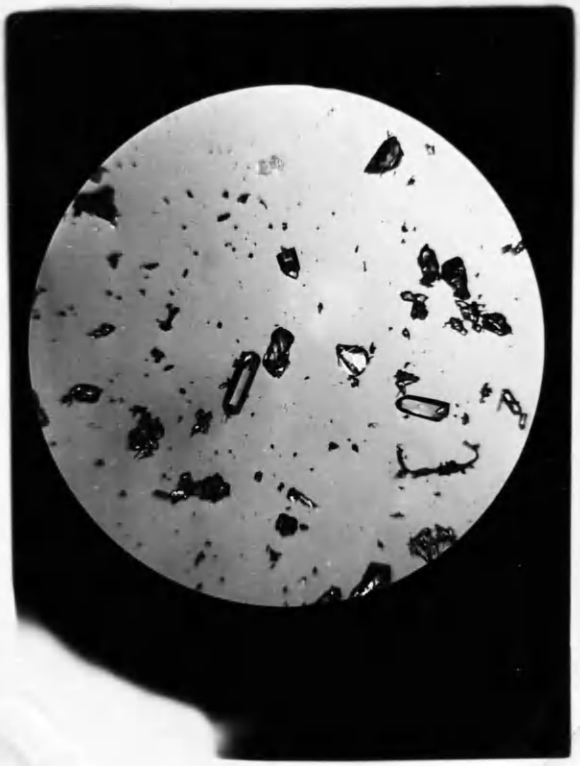


PLATE 13.

Product from quartz synthesis run. (Magnification x 10)

PLATE 14.

Product from quartz synthesis run. (Magnification x 10)

TABLE VI.

Solubility of Synthetic Quartz[*]

Mass-to-liquid ratio : 1 g. SiO_2/40 ml. borate buffer (pH 7.5)

Solution period : 24 hours at 37°C.

Dust	Colorimeter Readings	Solubility mg./100 ml.
Pure Synthetic Quartz	68 dil. 1:1[@]	(1.18 x 2) 2.36
" " "	78 dil. 1:1[@]	(1.36 x 2) 2.72
Synthetic Quartz prepared from Vitreosil rod + 0.5% aluminium powder	42.5	0.74
Synthetic Quartz + accidental impurities	44	0.76
Natural Quartz (Madagascar 50-70 mesh HCl cleaned)	5.0	0.1

[*] See Appendix 1 for molybdenum blue method of silica analysis.

[@] These solutions had to be diluted to bring their colours within the range of the EEL colorimeter.

From these results it is seen that there is considerable difference between the solubilities of the quartz prepared under similar conditions. This indicates the necessity for strict control over all operations so that reproducible results may be obtained:-

(1) The pressure should be strictly maintained, allowance being made after each run for the decrease in volume due to deposition on the walls of the vessel.

(2) The weight of source material should be as nearly as possible the same in every run.

(3) Quenching ought to be carried out at exactly the same temperature every run.

(4) Conditions for washing the products free from sodium metasilicate and sodium oleate, and the subsequent drying, should be identical, and the washing must be thorough.

It can be seen also that although the solubilities of the various pure quartz specimen are so different, the solubilities of the dusts containing impurities either deliberately or accidentally added are very much less than those of pure quartz specimens. All the synthetic quartz dusts have a very much higher solubility than the natural quartz of similar particle size.

Conclusions.

A method for the preparation of small crystals of synthetic quartz has been established. The introduction of impurities into the synthetic quartz should offer little difficulty considering the trouble involved in preventing contamination of the quartz.

Considerable difficulty may be experienced, however, in controlling the amount of impurity introduced, since it does not follow that all the material (e.g. alumina) placed in the autoclave will be incorporated into the quartz. It will also be difficult to determine whether that impurity which has been included is (a) localised in one part of the crystal crop, (b) distributed regularly throughout it, or (c) distributed periodically throughout.

The following programme of work is suggested:-

(1) The preparation of a stock of pure synthetic quartz to serve as a basis of comparison for other materials.

(2) The preparation of quartz containing varied amounts of deliberately added impurities which might be expected to occur in natural quartz (e.g. Fe, Al, Cr, Cu, Mn) and the investigation of the solubility, adsorptive capacity, etc., of these materials.

(3) The preparation of quartz containing more than one added impurity, and the examination of its properties.

(4) The natural genesis of quartz must occur under different conditions of temperature and pressure, and the effect of the variation of these on the solubility and pathogenicity could readily be investigated by the synthesis of quartz at various temperatures and pressures (to a maximum pressure of 1,000 atmospheres at 360°C. for the autoclave).

(5) In view of the carbon dioxide theory of silicosis (see Introduction, page 20) it would be of interest to prepare quartz in various different atmospheres and examine the effect on its physical and chemical properties.

(6) The presence of a "high-solubility layer" on the synthetic quartz would be of interest, especially since it has not been subjected to any grinding or polishing action.

(7) The various synthetic quartzes could be used for animal tests if the preliminary tests warranted.

could [illegible] be ground.

(8) The presence of [illegible] groups at the surface of finely ground quartz of various sizes [illegible] possible. The reagent 4,4'-[illegible]-dimethylaminotriphenylcarbinol could be used for this.

4. Comparison between Silica and Rutile.

No cases of pneumoconiosis have been reported amongst workers handling titanium oxide in the very fine and very pure form in which it is used as a pigment ([illegible]). In the light of the results obtained it would be interesting to determine whether or not titanium oxide is fibrogenic. This could be done by animal experiments with [illegible] of fine titanium oxide, a solution of $Ti(OH)_4$, or a neutral [illegible] a titanate.

The [illegible] should be [illegible]

Suggestions for Future Work.

1. The Ageing of Siliceous Dusts.

It would be interesting to investigate the following subjects:-

(a) The change in the nature of the surface of a freshly polished quartz crystal.

(b) The ageing of film of silica formed by evaporation. In electron microscopy some materials have been shown to alter their physical form considerably after evaporation on to a grid.

(c) The presence of atomic oxygen at the surface of finely ground quartz at various times after grinding. The reagent 4:4':4"-(dimethylamino)triphenylmethane could be used for this.

2. Comparison between Silica and Rutile.

No cases of pneumoconiosis have been reported amongst workers handling titanium oxide in the very fine and very pure form in which it is used as a pigment (56). In the light of the results obtained it would be interesting to determine whether or not titanium oxide is fibrogenic. This could be done by animal experiments with a suspension of fine titanium oxide, a solution of $Ti(OH)_4$, or a neutral solution of a titanate.

The comparison should be extended to cover other materials of interest such as ferric oxide (known to be fibrogenic) and alumina, (which is used in aluminium therapy). Materials whose crystalline habit is similar to that of silica should be included in the study.

3. The Effect of Trace Impurities on the Properties of Quartz.

The programme outlined previously should be carried out.

(i) [illegible]

[illegible]

Blue colorimetric, [illegible] (99), [illegible] (10), and [illegible]

[illegible] (?).

The method is based upon the reaction of silica with ammonium molybdate at suitable pH values to form the yellow silicomolybdic acid. Reduction of this yellow acid produces a blue colour, the intensity of which, when produced under standard conditions, may be calibrated against silica concentration.

(ii) Preparation of Reagents. The following standard reagents were employed.

A. 5% Ammonium Molybdate Solution. 20 ml. of 6N H_2SO_4 is added with stirring to a filtered solution of ammonium molybdate (6 g.) ($(NH_4)_6Mo_7O_{24}.4H_2O$) (Analar) in 100 ml. of distilled water.

B. Reducing Solution. Sodium sulphite (6 g.) ($Na_2SO_3.7H_2O$) (Analar) and hydroquinone (1 g.) are dissolved in 50 ml. of distilled water.

APPENDIX 1.

Estimation of Silica in Solution.

(i) General. The method employed for estimating the amount of silica in solution was a modification by Clelland (46) of the molybdenum blue colorimetric method of Isaacs (79), King (80), and Harrison and Storr (81).

The method is based upon the reaction of silica with ammonium molybdate at suitable pH values to form the yellow silicomolybdic acid. Reduction of this yellow acid produces a blue colour, the intensity of which, when produced under standard conditions, may be calibrated against silica concentration.

(ii) Preparation of Reagents. The following standard reagents were employed.

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B. Reducing Solution. Sodium sulphite (6 g.) ($Na_2SO_3.7H_2O$) (Analar) and hydroquinone (1 g.) are dissolved in 50 ml. of distilled water.

(iii) Test Solution. The "unknown" solutions were obtained from the tests as follows:-

(a) From tests using dusts of large particle-size which settled rapidly by simple decantation.

(b) From tests using dusts of small particle-size which formed suspensions with the borate buffer by centrifuging for 5 minutes at 3,500 r.p.m. and filtration through a Ford Sterimat Grade SB filter pad.

(iv) Method. 25 ml. of the silica solution to be estimated is pipetted into a Lusteroid (cellulose acetate) (82) tube. To this is added 18 ml. of distilled water (total volume 43 ml.) 2 ml. of solution A is added. The solution is stirred for 30 seconds with a cellulose acetate spatula, and the yellow colour of silicomolybdic acid is then allowed to develop for a further 4.5 minutes. When this development is complete, 5 ml. of solution B is added, the mixture is again stirred for 30 seconds, and the resulting blue colour allowed to develop for 30 minutes. The intensity of the fully developed colour is finally measured using an EEL colorimeter (83) using a red filter (Ilford No. 608).

(v) Accuracy. For maximum accuracy it is essential to adhere strictly to standard development times. To eliminate error in this factor when carrying out a series of estimations the following method was used. All the reagents were measured out in a series of tubes equally spaced in a rack, and could thus be added simultaneously to the silica solutions in Lusteroid tubes held in a similarly spaced rack. The solutions were stirred by a series of correspondingly spaced spatulas fixed combwise to a holder.

The EEL colorimeter has a logarithmic scale, and the overall accuracy of the method depends upon the part of the scale on which the reading falls. Maximum accuracy (±2.0%) is obtained at scale readings between 30 and 60.

(vi) Calibration Curves. A standard silica solution was prepared by fusing a weighed amount of finely ground quartz with sodium carbonate in a platinum crucible. The cooled melt was dissolved in distilled water and, after neutralisation with sulphuric acid, made up to a known volume.

The calibration curves were obtained by adding measured volumes of this solution to 25 ml. of borate buffer and making up to 43 ml. with distilled water. The estimation is then carried out as described above, and points on the calibration curve obtained.

(vii) Units. Solubilities are expressed throughout as the concentration of the silica solution produced under the stated experimental conditions (mg. SiO_2/100 ml. solution).

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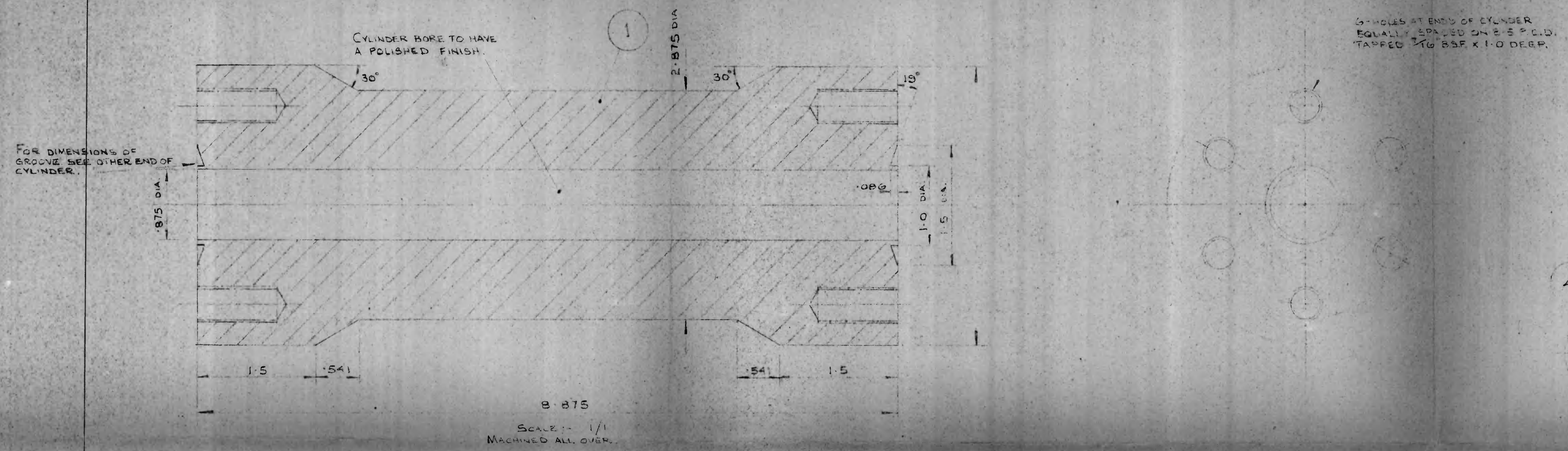
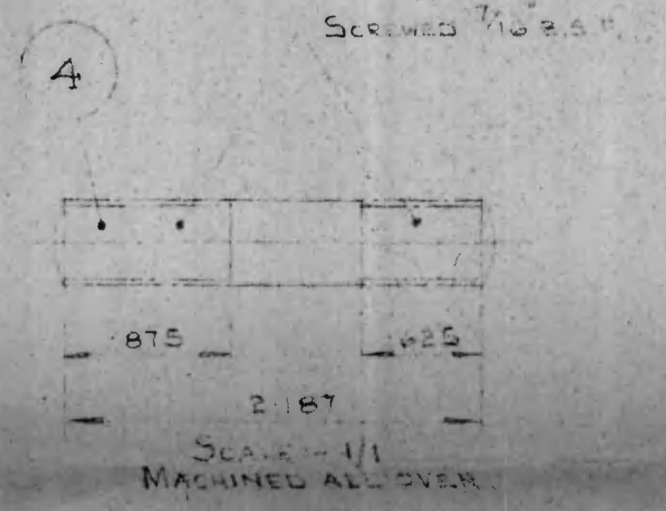
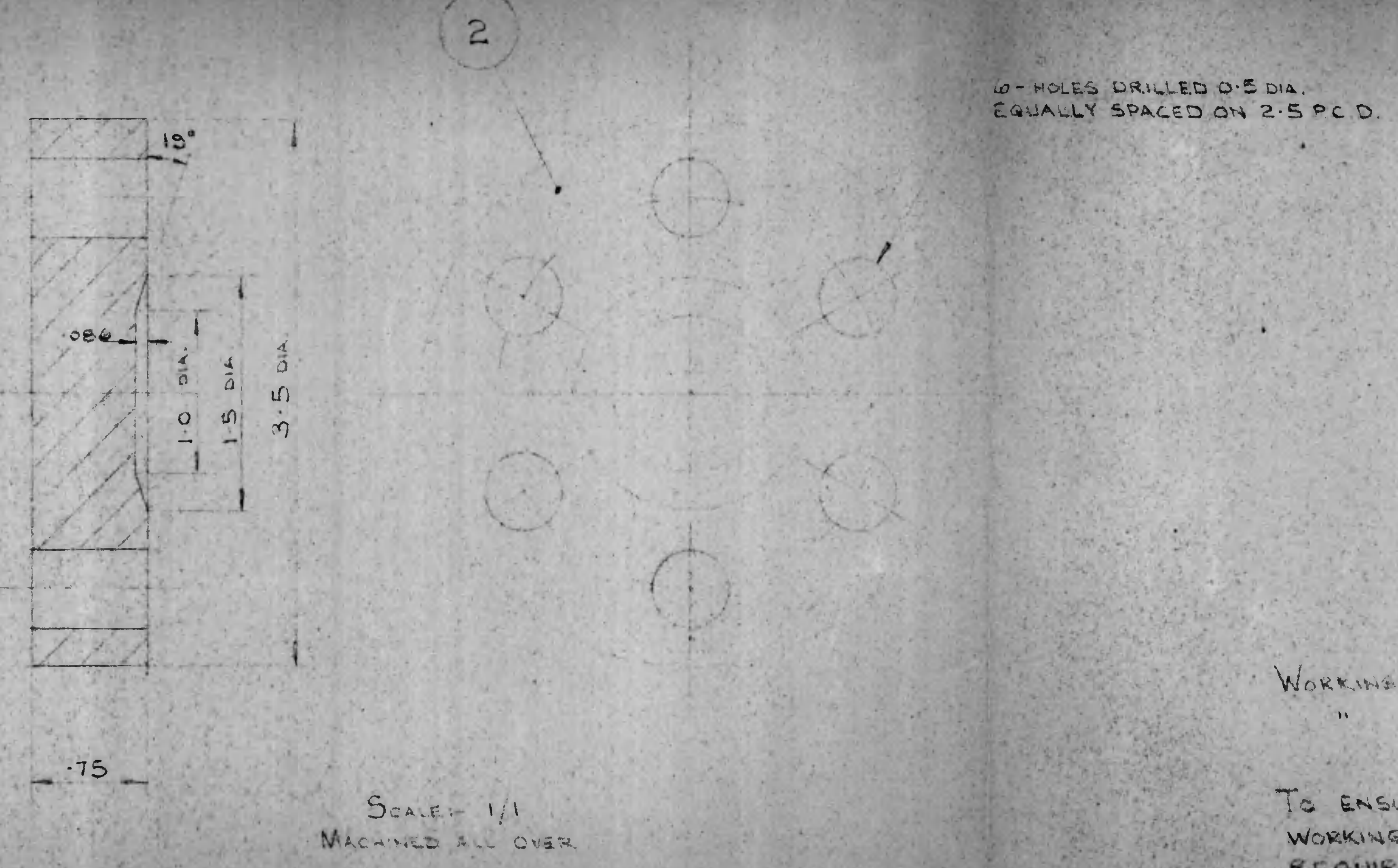
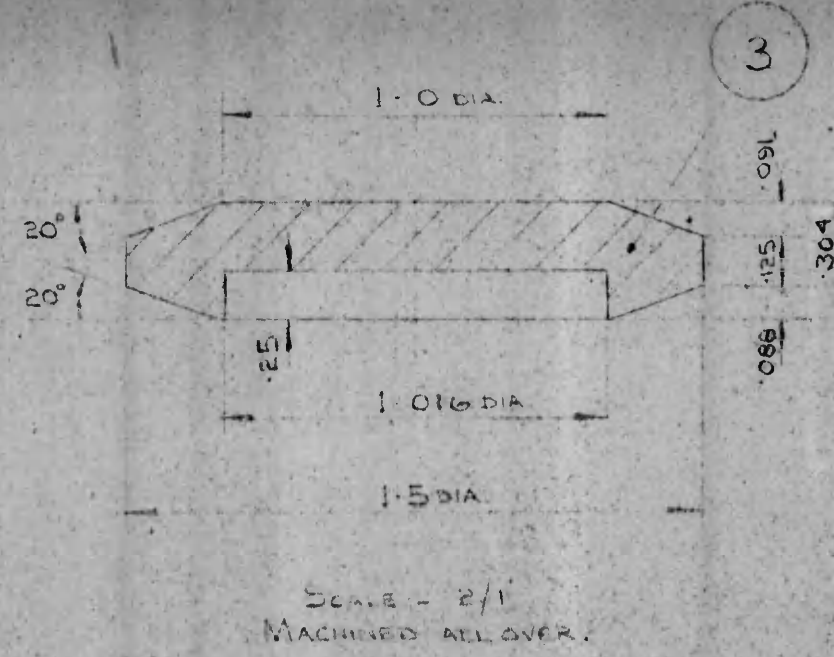
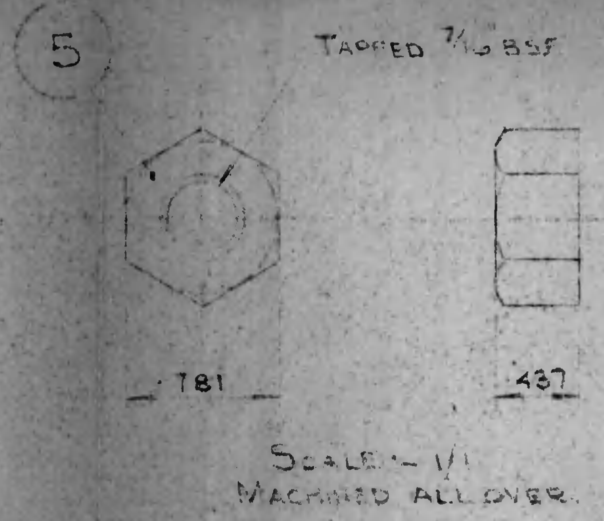
THIRD ANGLE PROJECTION











REF. No.	DESCRIPTION.	MATERIAL		No. REQD.
1	CYLINDER.	HIGH TENSILE STEEL	UTS 50-60 TONS/□"	1
2	FLANGE	"	"	2
3	LENS RING.	"	"	2
4	STUD	"	"	12
5	NUT.	"	"	12

WORKING PRESSURE :- 15000 LBS/SQ. IN
" TEMPERATURE :- 370°C

TO ENSURE A GOOD METAL TO METAL JOINT AT THE ABOVE WORKING FIGURES, A VERY SMOOTH MACHINING FINISH IS REQUIRED ON LENS RING FACES AND GROOVES IN CYLINDER ENDS.

ALL DIMENSIONS IN INCHES.

NATIONAL COAL BOARD
SCOTTISH DIVISION
SCIENTIFIC DEPARTMENT
EDINBURGH.

DETAILS OF AUTOCLAVE

SCALE	AS SHOWN.	
DRAWN B	A	21·1·55
TRACED B		
DRAWER NO.	D1	

DRG. No. D66