THE COMPOSITION AND, IN PARTICULAR, THE DISINFECTANT VALUE OF THE PHENOLS IN COAL TARS FROM VARIOUS SOURCES

by

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SUMMARY

The literature on the subject of disinfection with phenolic bodies is very extensive but much the greater part of it is concerned only with the lower boiling fractions of the phenols from which phenol and the cresols, in a pure state, may be isolated with comparative ease. The object of the present research is to examine the phenols of higher boiling points, from which few pure products have so far been isolated, in order to determine whether knowledge of their disinfectant value in addition to known physical constants will assist in distinguishing, or proving relationship, between phenols from different sources such as from low temperature or high temperature coal-tars.

Owing to the low solubility of the high boiling phenols in water it was necessary to employ them in an emulsified form. Methods of emulsifying the phenols were studied and comparisons were made between the disinfectant value and the average size of the emulsion particles, in order to obtain the most efficient type of preparation and to determine the extent of variation of the disinfectant value with alteration in the emulsion particle size.

The disinfectant values were determined by the Rideal-Walker method and, during the progress of the work, one cause for inconsistent results was traced to the relatively inaccurate method of standardising the broth culture medium.

Slight variations in the acidity of the broth were found to change the phenol coefficient value of the same disinfectant preparation and, after publication of the results, the official method of standardising the broth was revised.

The comparison of the phenols from different sources of tar was commenced after ascertaining the best methods to obtain consistent results for the disinfectant values of the phenols. In the comparison, identical fractions of the phenols from four tars were prepared and the disinfectant values of the fractions were compared with those of pure phenols.

The results of the research work are presented under the following four headings:-

(1) Introductory review of literature.

(2) Preparation of disinfectant emulsions and comparison of their germicidal power with emulsion particle size determinations.

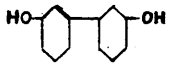
(3) Effect of slight variation in the adjustment of the acidity of Rideal-Walker broth upon the phenol coefficient value of coal-tar disinfectants.

(4) Comparison of the disinfectant value of the phenols from different sources of tar.

PART I

INTRODUCTORY REVIEW OF LITERATURE

Relative Germicidal Power of Phenols.

Previous work on the disinfecting action of homologous phenols shows that the disinfectant value, or germicidal power, is increased when one or more methyl groups are introduced into the phenol nucleus,[1] or when a methyl group is replaced by an alkyl radicle of greater molecular weight.[2] Phenols of higher disinfectant value are also obtained when the molecular weight is increased as in the naphthols, or in the products formed by the linkage of two phenol groups, either direct, or through the groupings CH_2, CHOH, and CHOR,[3] e.g:- 

The relatively greater germicidal efficiency of the cresols and higher phenols is usually expressed as a ratio, termed the phenol coefficient value, in which phenol is the standard of comparison and is given the value of unity. Cooper (B.M.J., 1912, I, 1234), to cite one example, found the phenol coefficient values of o- m- and p-cresol to be

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[1] Z. Physiol. Chem. 1906, 47, 173. H. Bechold & P. Ehrlich.
Bagliani, Z. Allgemein. Physiol. 1904, 3, 313.
F. L. Pyman, J.C.S. 1917, 111, 1103.
P. May, "The Chemistry of Synthetic Drugs" 152, 3rd Edn., London, 1921.
S. Rideal & E. K. Rideal, "Disinfection & Sterilisation", 234, London, 1921
S. Fränkel, "Die Arzneimittel-Synthese" 70. 549, 6th Edn. Berlin, 1927.
F. Ishiwara, Z. Immunitats, 1924, 40, 429.

[2] Fränkel, ibid, 543. Rideal & Rideal, ibid, 236.
K. Laubenheimer, "Phenol und seine Derivate als Desinfektionsmittel" Berlin, 1909.

2.6 and thymol 25 when an aqueous solution of the phenol was tested against Bacillus Typhosus. The phenol coefficient is variable to some extent, depending upon the technique of the test and the micro-organism upon which the disinfectant acts. Cooper (ibid), employing the same technique, found the phenol coefficient values of o- m- and p-cresol to be respectively 2.1, 2.0, and 2.4 when Staphylococcus Pyogenus Aureus was the test organism.

Technical Phenolic Emulsions.

The main practical difficulty encountered in the use of the phenols is the very slight solubility of the members of the series above phenol and this has necessitated the use of hydrotropic or emulsifying agents to increase their solubility. Caustic soda solution, sulphuric acid, organic sulphonic acids, soaps and protein solutions have all been applied and the patent literature is quite extensive.(4) Soaps, however, from the point of view of relative efficiency and cheapness, have much the widest application and

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[2] T. B. Johnson & F. W. Lane, J.A.C.S., 1921, 43, 348. V. Leonard, J.Am.Med.Assoc., 1924, 83, 2007.

[3] Bechold & Ehrlich, ibid. Rideal & Rideal, ibid, 246.

[4] Lunge, "Coal Tar & Ammonia" 2, 807, 5th Edn., London, 1916. Ullmann "Enzyklop. der Tech. Chem." 3, 702, Berlin-Wien, 1916.

disinfectant fluids are readily prepared by solution of the soap in the phenols alone or in a mixture of phenols and hydrocarbon oils. The commercial product lysol is formed by the combination of one volume of a mixture of the isomeric cresols with an equal volume of a concentrated soap solution. Lysol, or cresol-soap solution, is an official preparation in the pharmacopoeas of most countries and gives a clear solution in all proportions of water, this result being due to the increased solubility of cresol in soap solution (Bailey, J.C.S., 1923, 123, 2579). The higher phenols, according to Cooper (B.M.J., 1912, I, 1234, 1293, 1359), require a greater proportion of soap and on addition to water give turbid solutions, or emulsions. The combination of hydrocarbon oils with the higher boiling phenols and soap, improves the stability and appearance of the emulsions formed in water and reduces the cost of the preparation. The method is in general use for the emulsification of the higher phenols and preparations of this type are known as soap fluids, or black fluids. The name of white fluid is applied to stable emulsions of the phenols in protein solutions.

Increase in Germicidal Power of Phenols by Emulsification.

It has been frequently demonstrated that the phenols are more active germicidally in the emulsified form than in solution. Chick & Martin (J. Hyg. 1908, 8, 698) found

a sample of tar acids to disinfect 7.5 times more quickly when in the emulsified form. They explained the increase in efficiency by the process of adsorption, the bacteria being surrounded by the disinfectant in greater concentration than that present in the bulk of the liquid. Chick (J. Hyg. 1908, 8) found that all types of particulate organic matter, e.g., animal charcoal, dust, finely precipitated coagulated albumen, bacteria, or faeces, had similar though not equal adsorptive effects. The addition of faeces along with bacteria reduced the phenol coefficient values of phenolic disinfectants, owing to the competitive adsorption of the tar acids by the faeces. The reduction was greater with an emulsion disinfectant than a soluble disinfectant, and was more pronounced with a fine emulsion than a coarse emulsion. The latter result indicates that the fineness of the emulsion may have an important bearing upon the germicidal power of phenolic disinfectants, and this view is expressed by several writers, as follows:-

R. T. Hewlett, ("A Manual of Bacteriology, Clinical and Applied" 774, Churchill, London, 1921), "The efficiency of coal tar emulsion disinfectants varies with the character of the emulsion as well as the active ingredient."

S. Rideal and E. K. Rideal,("Disinfection and Sterilisation" 293) "It is well known that with the emulsified tar acid disinfectants the enhancement of germicidal activity with the dispersity of the emulsion is by no means

inconsiderable, and the aim of manufacturers is to produce a fine emulsion."

E. K. Rideal, ("5th Report on Colloid Chemistry" 37, H.M. Stat. Office, London, 1923), "In the preparation of the emulsified disinfectants the germicidal power for a given tar acid content is nearly proportional to the fineness of the emulsion."

Action of Soaps in increasing the Germicidal Power of Phenolic Emulsions.

The soap employed in the preparation of the emulsion may increase the germicidal action in addition to presenting the disinfecting phenols in the more serviceable emulsified form. Cooper (ibid) found pure cresylic acid to have a phenol coefficient of 2.5 in the emulsified form compared with 2.2 in aqueous solution. He attributed the increase in the coefficient value of emulsified cresylic acid to the soap, since at the particular dilution of 5 in 1000 the cresol would be in solution. Fränkel (ibid 542) is of the opinion that the strengthening action of soaps upon antiseptics rests, not on a mutual influence of the substances in solution, but upon the primary action of the soap upon the bacterial cell which enables the antiseptic to display a more intensive action. H. Kenwood (M.O., 1926, 35, 121) expresses the view that the action of oil globules in a weak soap solution is to draw soap by surface adsorption to the surface of the oil globules. By this

means there are obtained oil globules having on their surface a strong solution of soap which, in the case of disinfectant emulsions, contains the higher boiling tar acids in solution owing to their greater solubility in soap, and these oil globules float about in virtually pure water. The further suggestion is made that a microbe, coming in contact with this strong soap solution, gets into a zone of high osmotic pressure and the high boiling acids in solution are forced into the body of the microbe, which is at a lower osmotic pressure. E. Putter (Klin. Wochschr., 1923, 2, 888, 936) advances a simpler explanation which depends on the phenol soap-solutions containing most of the phenol in colloidal aggregates. If bacteria are added, some of the molecularly dissolved phenol will pass into the bacteria and molecular phenol diffuses from the aggregates until equilibrium of the three phase system is established.

Relative Efficiency of Different Soaps.

The disinfectant action of soaps has been studied by several workers and most recently by J. E. Walker (J. Inf. Dis. 1924, 35, 557; 1925, 37, 181; 1926, 38, 127;) but their germicidal strength is low and alone could not account for the increased germicidal value of phenol compounds in presence of soap solution. The action of different soaps on phenols has been studied by the following authors:-

Rapp (Desinfektion, 1909, 2, 643/670; Centr., Bakt. Parasitenk., Abt. I, Ref., 1910, 45, 681) found cresols to be more effective germicides when emulsified with linseed-oil soap and palmitic acid soap than when emulsified with soaps of oleic or stearic acids. Addition of rosin soap was found to increase the germicidal powers of saponified cresols.

J. M. Schaffer (U. S. Dept. Agri. Bull., 1920, 855, 1/5) observed that rosin soap-cresol preparations had a slightly higher germicidal value than those containing only vegetable— or fish-oil soaps.

F. W. Tilley and J. M. Schaffer (J. Inf. Dis., 1925, 37, 359) prepared cresol-soap mixtures with cocoanut-oil and linseed-oil soaps; the former gave much higher germicidal values and this distinction was most marked with the higher boiling phenols. Mixtures containing about one-half as much soap as cresol showed the maximum efficiency.

Cooper (B.M.J., 1912) prepared cresol-soap mixtures with soft soap, linseed-oil soap, rosin soap and castor-oil soap. The castor-oil soap preparations gave the best results. From a number of emulsifying agents which were experimented with, the castor-oil soap proved the most suitable and was indeed the only agent which formed permanent stable emulsions with high boiling tar acid fractions.

These results show very clearly that all soaps do not act alike for the emulsification of cresols, or higher phenols.

Theories of Disinfection.

S. and E. K. Rideal (Disinfection and Sterilisation, 182/195) and E. K. Rideal (5th Colloid Report, 31/38) discuss extensively the many factors which influence germicidal activity, but no general theory of disinfection, applicable to ionized and non-ionized solutions, emulsions and other colloidal systems, has yet been advanced. The factors which are effective include precipitation of the baterium by an oppositely charged ion or colloid particle and adsorption, followed by penetration of the disinfectant. The degree of penetration is influenced by the partition coefficient K of Overton and Meyer ("Studien uber Narkuse", 1901; Proc. Roy. Soc., 1915, 389), where K = solubility in lipoid ÷ solubility in water. An effective agent should show a high value for K, to enable it to dissolve readily in the lipoid material of the bacterial cell, and numerous investigators have traced such a connection between antiseptic and disinfectant action and lipoid solubility. Other factors which determine the primary adsorption are probably of greater importance than the lipoid solubility coefficient and perhaps the chief among these are substances

which reduce the interfacial tension between the bacterium and the medium in which suspended. Such substances, in accordance with Gibb's equation, cause the surface concentration on the bacterial interfacial surface to exceed the bulk concentration. In the benzene hydroxyl series it has been found that surface tension, which is assumed proportional to the interfacial tension at the bacterial surface, and the germicidal value, decrease in the following order:- thymol, camphor, menthol, cresols, phenol, resorcin, hydroquinone, phloroglucinol, pyrogallol. The view that adsorption is a chemical process and that reaction occurs between reactive groups in the adsorbed material and acceptor reactive groups in the micro-organism, is of assistance to the theory of disinfection by suggesting a reason for the decided specificity of certain agents towards a class of organisms or even a single organism.

Cooper (Biochem. J., 1912, 6, 362; 1913, 7, 175) investigated the process of disinfection by phenols and found that the germicidal and protein precipitating powers of phenol were similarly affected by the entrance of various chemical groups into its molecule. He concluded from the effect of various factors on the two apparently parallel processes that "The adsorption of phenols by bacteria is merely the initial stage in the process of disinfection, and that the germicidal action which follows is due, not to

a typical chemical union of the phenols with the bacterial protoplasm, as appears to be the case with Formaldehyde, but to a de-emulsifying action upon the colloidal suspension of some constituent protein, or proteins, essential for the vitality of the organism." The germicidal action of phenols is also similar to disinfection by heat, which Chick (J. Hyg., 1910) found analogous to the heat coagulation of proteins. Following a suggestion of Moureau and Dufraisse (Z. Angew, Chem., 1925, 267) that the strong biological action of the phenols depends upon their anti-oxygenic activity which prevents the uptake of oxygen in the living organism, K. Schubert and K. Richter (Centr. Bakt. Parasitenk., II Abt., 1926, 66, 11) have carried through a series of experiments on the germicidal action of low and high boiling phenols against aerobic and anaerobic cultures. Their results lead them to suggest that the germicidal action of the higher boiling phenols rests principally on their reducing action by which oxygen is removed both from the medium and the bacterial cell, thereby causing injury to the conditions of life of the organism.

Kronig and Paul (1897), Madsen and Nyman (1907), Chick (1908), Lee and Gilbert (1918) and other authors have studied the process of disinfection from the purely physico-chemical standpoint and have shown that in many respects the process is analogous to a chemical reaction, the disinfectant

representing one reagent and the protoplasm of the bacterium the other. By this theory disinfection is an orderly time process and follows the law of a monomolecular reaction, as the disinfectant is in so great excess, comparatively, that its concentration may be regarded as unaltered during the process. The process resembles further a chemical reaction in that increase in temperature greatly augments the velocity of disinfection, but with phenol and the emulsified disinfectants the reaction velocity temperature coefficient is higher than normally found for chemical reactions and the logarithmic relationship between the velocity of reaction and the concentration of the disinfectant is more complex than a chemical reaction of the monomolecular type. Opposed to this mechanistic view there is a vitalistic conception, or theory of permanent resistance, which postulates that the progressive nature of the disinfection process is accounted for as being due to a type of biological variation, namely, permanent differences in the degree of resistance possessed by the various individual micro-organisms of a pure culture.

Standardisation of Disinfectants.

An excellent historical resume of the advance in the technique of standardising disinfectants has been prepared by S. Delepine (Royal Instit. Pub. Health, 1908; J.S.C.I.,

1911, 30, 334). All methods are classified into two groups, one where the bacteria are protected from the direct action of the disinfectant and, therefore, the penetrating power of the disinfectant is of importance for efficient action, and the other where the bacteria are comparatively speaking in an unprotected state. Many factors have been found to influence the results of disinfectant tests and, according to Delepine, the following general conditions must be specified beforehand in any method:-

1. The kind of microbe used and its resistance to disinfection.
2. The age of the cultures.
3. The temperature of incubation.
4. The composition of the culture medium.
5. The number of microbes.
6. The quantity of associated material (in the first group of methods)
7. The duration of the exposure to the disinfectant in each set of comparative experiments.
8. The temperature of the disinfectant during exposure.
9. The means of arresting the action of the disinfectant at the end of the experiment.

Many tests have been suggested for the standardisation of disinfectants and, keeping the above points in view, there are to-day four distinct methods, viz:-

1. The Thread method.
2. The Garnet method.
3. The Inhibition method.
4. The Drop or Suspension method.

The classical thread method of Koch (1881) has been modified and improved upon by Fraenkel (Z. Hyg., 1889, 6.), Behring (Z. Hyg. 1890, 9.) and Delepine (J. Royal San. Inst., 1907, 28.). It derives its name from the mode of transferring the bacterial culture, viz., by the use of short lengths of thread which have been impregnated with a culture of the micro-organism and then dried at a suitably low temperature. Delepine classifies the method under the protected bacteria group.

Kronig and Paul (Z. Hyg., 1897, 25, 1.) modified Koch's method by introducing garnets in place of threads and employing a water emulsion of the bacteria in order to reduce the effect of associated substances. The garnet method has been used in the physico-chemical investigations on disinfection by the authors previously mentioned.

The inhibition method measures the antiseptic value of a substance rather than the disinfecting power. Browning and co-workers (B.M.J., 1917, I, 73) by this test found certain dyestuffs to inhibit the growth of specific organisms at very great dilution, a result which could not be anticipated from their phenol coefficients.

The chief of the drop methods is the Rideal-Walker Test (J. Royal San. Inst., 1903, 24.) and the technique depends on the introduction of a small measured volume of a broth culture of B. Typhosus into varying dilutions of the disinfectant and a control dilution of phenol. The phenol dilution is present as a control on the vitality of the organism. Definite times of contact between the disinfectant and the culture are permitted by the test before transplantations are made into sterile broth tubes, in order to determine whether or not disinfection has resulted. The use of specified materials for preparing the broth medium, accompanied by the use of phenol as a control standard, gave the test precedence over the previous drop methods of Blyth (Proc, Roy. Soc., 1886) and Sternberg ("Manual of Bacteriology" N.Y., 1893, 156). Slight modifications to the test have been made by the authors (Approv. Tech. of the R. W. Test, London 1921) but it is essentially the same, to-day, as when first submitted. The test has not met with universal approval, owing mainly to the discordancy in the results reported by different operators for the same disinfectant preparation, and the following modified forms of the test have been devised to improve upon it.

"Lancet Commission Method" (Lancet, 1909, 177, 1454, 1516, 1612; Brit. Pharm. Conf., July 1910, Pharm. J., 1910, 85, 155, 169).

"American Hygienic Laboratory Method"
Amer. Bur. of Hyg., Bull. No. 82, J.Inf. Dis., 1911, 8, 1.
Amer. Pub. Health Repts., 1921, 36, 1559. (revised method)

In addition Martin and Chick (J. Hyg., 1908, 8, 654), Wynter Blyth (J.S.C.I., 1906, 25, 1183), and the British Admiralty, have introduced methods of testing in which various kinds of associated matter are present, in order, it is claimed, to approximate more closely to practical conditions.

These modifications, in general, present no marked superiority over the Rideal-Walker technique and the American Hygienic Laboratory Test appears to have increased the labour and manipulative skill without a corresponding increase in efficiency. In addition, the inclusion of associated matter, not essential for the cultivation of the organism, is disadvantageous when comparing the structure of compounds with germicidal power as, by adsorptive action, it reduces the amount of the germicide taking part in the disinfection process. The results thus obtained do not represent the germicidal values of the weights of active materials added, but are a measure of the efficiency of the material unadsorbed by the associated matter, and even with closely related compounds the unadsorbed material is not necessarily the same.

On account of this disadvantage of associated matter

and because of the already successful application of the Rideal-Walker test to the standardisation of coal-tar disinfectants, it was decided to use this method of test alone throughout the present work.

PART II

PREPARATION OF DISINFECTANT EMULSIONS AND COMPARISON OF THEIR GERMICIDAL POWER WITH EMULSION PARTICLE SIZE DETERMINATIONS

PHENOLIC DISINFECTANT EMULSIONS

Introduction

There are two distinct types of phenolic disinfectant preparations, of high germicidal power, in commercial use at the present time and they are referred to as soap fluid, or black fluid, disinfectants and emulsion, or white fluid, disinfectants.

Soap fluid disinfectants are essentially solutions of soap in a mixture of phenols and hydrocarbon oils and they form stable emulsions when mixed with distilled or soft waters. In salt or very hard waters they do not emulsify unless the adsorption of the soap on the oil globules is first permitted to take place, either by preparing a concentrated emulsion in soft water and then diluting with salt water, or by adding the salt water gradually to the fluid. The percentage of phenols in the fluids seldom exceeds 40% and a large part of the phenol content must consist of the higher boiling phenols, where a disinfectant of high coefficient value is required.

The emulsifying agent in the emulsion type of disinfectant is a protective colloid of the nature of glue or gelatine, these emulsions may be mixed directly with soft, hard, or salt waters, without decomposing, and are in addition comparatively stable in urine. The high coefficient

emulsion disinfectants normally contain 50% to 60% of phenols, mainly high boiling tar acids containing little or no hydrocarbon oil, dispersed in an aqueous solution of the emulsifying agent.

It was decided to prepare disinfectant fluids of the two types and the preliminary work was conducted with a commercial sample of refined high boiling tar acids, in order that the results would have a practical value by themselves in addition to providing information for use later in the emulsification of the phenols from particular tars.

PREPARATION OF SOAP-FLUID DISINFECTANTS

THEORY

Many theories have been advanced to explain the formation and stability of emulsions and the following bibliography is abstracted from a paper by Griffin (J.A.C.S. 1923, 45, 1648).

1. Emulsification depends principally upon obtaining the proper surface tension and viscosity.
   Quincke, Ann., 1888, 35, 571.
   Donnan, Z. Physik. Chem., 1899, 31, 42.
   Donnan & Potts, Kolloid Z., 1910, 7, 208.

2. Emulsions consist of droplets of oil surrounded by a film of discrete, insoluble particles which are more easily moistened by water than by oil.
   Pickering, Kolloid. Z., 1910, 7, 11.

3. Emulsions are made by the dispersion of oil, not in a water solution of soap or other emulsifier, but rather in a hydrated colloid. Enough of the colloid must be present to bind all the water.
   Fisher & Hooker, "Fats and Fatty Degeneration" N.Y., 1917.

4. Emulsions consist of droplets of oil which are surrounded by more or less plastic films.
   Bancroft, "Applied Colloid Chemistry" N.Y., 1921.
   Briggs, J. Phys. Chem., 1915, 19, 210.
   Holmes & Cameron, J.A.C.S., 1922, 44, 66.
   Clark & Mann, J. Biol. Chem., 1922, 52, 157.

5. Emulsions consist of droplets of oil in water, with an interface composed of molecules of a third substance, the molecules being so orientated that the group which has an affinity for water is dissolved in the water, while that which has an affinity for the oil is dissolved in the oil.
   Langmuir, J.A.C.S., 1917, 39, 1848.
   Harkins, Davies & Clark, ibid, 1917, 39, 541.

The conditions which are essential seemingly for the production of a stable emulsion are that the globules must be so small that they will remain suspended, and that the emulsifying agent must go into the interface and produce a film having satisfactory physical properties, e.g., plasticity.

The soaps of the alkali metals have proved excellent emulsifying agents for oil-in-water emulsions, as they are strongly adsorbed at the interface and are not peptised markedly by oil; they conform with the simple general formulation of Briggs (cf. Bancroft, "Applied Colloid Chem." N.Y., 1926, 352) that an oil-in-water emulsion is produced if the emulsifying agent at the interface is chiefly in the water phase and a water-in-oil emulsion if the emulsifying agent at the interface is chiefly in the oil phase. The soap does not go entirely into the interface in emulsions but, as Briggs (J. Phys. Chem., 1915, 19, 210) has shown with sodium oleate/benzene emulsions, it distributes itself between the interface and the continuous water phase. The amount of soap adsorbed at the interface is entirely dependent on the peptising action of the water (Bancroft, ibid, 357), anything which decreases or increases the peptising action of the water on the soap will respectively increase or decrease the soap at the interface. Griffin (J.A.C.S., 1923, 45, 1648) has determined that the quantity

of soap adsorbed in mineral oil-soap emulsions is proportional to the area of the interface formed and is not dependent upon the concentration of soap originally in the solution; stable emulsions are formed only when the soap is sufficient to form an interfacial film of unimolecular dimensions round the oil globules. Riemann & van der Meulen (J.A.C.S., 1924, 46, 876; 1925, 47, 2507) found with toluene-phenol-sodium oleate or sodium ricinoleate emulsions that the soap in the interface increased with the soap concentration in the emulsion. The phenol in these emulsions, however, had entered the interfacial film to a limited extent in substitution for soap and their results were not in disagreement with a unimolecular film theory. Harkins and Zollman (J.A.C.S., 1926, 48, 69) studied the effect of interfacial tension on the emulsification of benzene in sodium oleate solutions. It was observed that when the interfacial tension between the benzene and sodium oleate was below 10 dynes/cm the benzene emulsified easily in the aqueous phase, when below 1 dyne it appeared to emulsify spontaneously. The interfacial tension was decreased by the addition of sodium hydroxide, or sodium chloride, particularly by a mixture of the two, also by oleic acid.

EXPERIMENTAL

Sodium and Potassium Oleates as the Emulsifying Agents

The materials employed in the preparations were as follows:-

1. Commercial High Boiling Tar Acids (Wm. Baird & Co., Glasgow).

The sample was dark yellowish-brown in colour and smelled slightly of sulphuretted hydrogen. The distillation test given below was carried out by distilling 100 cc of the sample from a 200 cc Wurtz flask (Jena), enclosed in an asbestos box and connected to an air condenser. The average rate of distillation was 1 drop per second and the distillation was stopped at 230° C. and the condenser tube drained. The specific gravity was taken with a Westphal balance. The hydrocarbons represent the residue from the solution of 1 part of the phenols in 4 parts 9%-NaOH; two results are given, one where the hydrocarbons were permitted to settle from the solution and the other where they were removed by solution in petroleum ether.

Sp. Gr. 15.5° C	=	1.032.
Hydrocarbons (9% NaOH)	=	5.75% (By settling)
		9.30% (By pet. ether extraction)
Distillation Test (100 cc.)		I.P 205/210° C

	Water	= 0.8%
Dist. @	215°C	- 4.5%
	220	20.5
	225	35.5
	230	49.8 (Drained)
	240	61
	250	71
	260	78
	280	86
	300	92
	317	96.6% (Drained)

2. Blast-Furnace Neutral Oil.

The neutral oil was obtained by washing a sample of blast-furnace creosote oil (Wm. Baird & Co., Glasgow) with 9%-sodium hydroxide until no further increase in the volume of soda added was noted, and then with 18%-sodium hydroxide until certain that all phenols were completely extracted. The following are the physical constants for the creosote and neutral oils:-

		B. F. Creosote Oil	B.F. Neutral Oil
Sp. Gr. 15.5°C		0.9744	0.9476
Tar Acids - 9% NaOH		26%	Nil
18% "			Nil
Yield of neutral oil			70%
Distillation Test -	I.P.	195°C	197°C
(100 cc.)	Water	0.7%	0.1%
	Dist. @ 210°	1.5%	
	215	3.0	1.0
	220	7.0	2.0
	225	12.0	4.0
	230	19.5	6
	240	33	11.
	250	42	22
	260	49.5	31
	280	65	54
	300	76	69
	320	84.5	80.5
	340	90	87.5
	360	95.0	94.0

3. Oleic Acid

Sample commercial oleic acid.

Sp. Gr. 15.5°	0.9037				
Acid Value	(1) 195.1	(2)	195.4	Mean =	195.3
Iodine Value (Hanus)	82.92		83.25	" =	83.1

Experiments were first made to determine the amount of sodium oleate soap required to form a stable fluid and emulsion with 50 c.c. of a mixture of equal proportions of high boiling acid and blast-furnace neutral oil. Additions of neutral 70%-sodium oleate up to 40% by weight of the oil mixture were made without satisfactory result, as the fluids which were formed did not emulsify readily in water. Drop number experiments with the oil mixture and sodium oleate solutions showed that the interfacial tension decreased with increasing concentration of soap, but variation in the concentration of the sodium oleate added to the oil mixture was not found to have beneficial effect. The results indicated that neutral sodium oleate alone did not reduce the interfacial tension sufficiently to make the fluids emulsify spontaneously in water, and it was decided to try whether the presence of free sodium hydroxide or free oleic acid in the fluids would assist emulsion formation. The use of free sodium hydroxide was tried first and fluids were prepared by the following method:-

20 c.c. high boiling acid and 20 c.c. B.F. neutral oil were measured into a bottle fitted with a glass stirrer and

reflux condenser. The bottle was partly immersed in a boiling water bath and the contents stirred at a steady rate of 250 revolutions per minute. The oleic acid was added and stirring continued for three minutes. The calculated amount of sodium hydroxide was then added, one drop every 5 seconds, and agitation continued for 15 minutes.

Three fluids were prepared by the above method containing 10% more than the theoretical amount of 25%-NaOH required to neutralise the oleic acid, which represented 12½%, 20% and 37½% of the oil mixture, but better results were not obtained. In order to obtain proper comparison, however, it was found necessary at this stage to have a simple and rapid method of comparing the stability of the emulsions produced and the following standard method was adopted:-

Emulsions were prepared in every case as 10% dilutions, by diluting the fluid under examination to ten times its volume with water, as follows:- 10 c.c. of the fluid were added to 90 c.c. distilled water, contained in a 100 c.c. stoppered cylinder, and mixed by inverting the cylinder 20 times, at 5 second intervals. The cylinders were set upright and the rate of creaming of the emulsions was noted. The rate of creaming is decided by three factors, viz., the specific gravity of the oil phase, the viscosity of the dispersion medium, and the size of the emulsion particles.

The chief varient in soap emulsions with the same oil phase will be the emulsion particle size, provided the soap concentration does not vary greatly.

The three fluids prepared with increasing proportions of oleic acid were tested by the above method, the rate of creaming was greatest for the fluid containing the least soap and slowest for the fluid containing the most soap. None of the fluids emulsified readily, however, and as there was an apparent excess of soap in the third fluid it was decided to maintain the oleic acid constant and equal to 20% of the oil phase in subsequent tests.

The four fluids given in Table I were prepared by the above described method (p. 24). The results of settling tests with 10% dilutions of the fluids in distilled water are recorded in Table II. The best emulsion has evidently been produced by the neutral soap but the fluid dispersed so very slowly in water that sodium oleate cannot be considered a satisfactory emulsifying agent for the preparation of disinfectant fluids to be compared with commercial products.

Linseed-oil soap was found to give a similar result to sodium oleate, and improved results were not obtained later with potassium oleate or potash linseed-oil soap. Soaps prepared from castor oil were found to give better results than sodium or potassium oleates, and extensive experiments with this oil were therefore conducted.

TABLE I

Soap fluids prepared with sodium oleate

No.	Oil Phase	Emulsifying Agent	Remarks	Description of Fluid
1	20 cc.H.B.Acid 20 cc.B.F.Oil	10 cc.Oleic Ac. 4.1 " 25%-NaOH 4.1 " Water	10% excess NaOH	Clear, dispersed in water very very slowly
2	Do.	10 cc.Oleic Ac. 3.7 " 25%-NaOH 3.7 " Water	NaOH equal to Oleic Ac.	Do.
3	Do.	10 cc.Oleic Ac. 3.3 " 25%-NaOH 3.3 " Water	10% excess Oleic Ac.	Do.
4	20 cc.H.B.Acid 20 cc.Coke Oven Neutral Oil	10 cc.Oleic Ac. 3.7 " 25%-NaOH 3.7 " Water	NaOH equal to Oleic Ac.	Slightly turbid, hardly dispersed in water.

TABLE II

No.	Percentage cream separated from sodium oleate fluids diluted to 10 times their volume with water, after			
	24 hours	48 hours	72 hours	96 hours
1	?	18	17.5	17
2	92	84	78	73
3	88	73	60	46
4	?	10.5	10.5	10.5

SODIUM AND POTASSIUM CASTOR-OIL SOAPS AS EMULSIFYING AGENTS

Sample of commercial castor oil.

Colour - almost water white.
Sp. Gr. 15.5° C - 0.9660

Saponification Value	(1) 182.7	(2) 182.3	Mean	182.5
Iodine Value (Hanus)	82.6	83.1	"	82.9

Preparation of fluids by saponification of castor oil in admixture with High Boiling Tar Acids and Blast-Furnace Neutral Oil.

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20 cc. H.B. acid, 20 cc. B.F. neutral oil and 10 gms. castor oil were mixed in a bottle, fitted with mechanical stirrer and reflux condenser, and heated in a boiling water bath for fifteen minutes. A measured amount of 25% NaOH was then added and stirring was continued for 30/40 minutes. Samples of the fluid were withdrawn at 10 minute intervals and the progress of the saponification tested by adding the sample to water. The final fluids were clear, viscous and dispersed slowly in water forming pink-mauve coloured emulsions. No visible oil globules separated from these emulsions if the quantity of caustic soda solution used was equivalent to, or 10% greater than, the amount required for the saponification of the castor oil. These emulsions did not cream completely on settling, as in the case of the oleic acid preparations, but the larger particles alone separated to the surface, a permanent opaque emulsion and

not a transparent aqueous layer forming the lower part of the emulsion. The percentage of cream from 10% dilutions, after 48 hours settling, varied between 1% and 10% but this large variation was found to be due to the degree of saponification of the castor oil. The best results were obtained when excess sodium hydroxide was present, or when fluids containing the equivalent amount of sodium hydroxide were heated finally over an oil bath, in order to complete the saponification of the castor oil. Equally good results were more easily obtained, however, by the addition of fully saponified neutral castor-oil soap to the oil mixture, and this method was chosen for subsequent preparations.

Preparation of fluids by the addition of castor-oil soap to mixtures of High Boiling Tar Acids and Blast-Furnace Neutral Oil.

Neutral castor-oil soaps were prepared by saponifying 60 parts, 50 parts, and 44 parts by weight of the oil with the equivalent amounts of sodium or potassium hydroxide solutions and adjusting the weight of each finished soap to 100 with water. Fluids were prepared by heating a mixture of equal portions of the tar acids and neutral oil over a boiling water bath and adding the soap in small portions at a time until, on pouring a little of the fluid into water, a perfect emulsion was obtained from which oil globules did not separate.

The results of the preparation of fluids with equal proportions of H.B. tar acids and B.F. neutral oil, employing castor-oil soaps as the emulsifying agent, are summarised below.

(a) Castor-oil soaps, prepared with caustic soda or potash, dissolved readily in the mixture of phenols and hydrocarbon oils. The amount of soap required in order to form a disinfectant fluid which emulsified evenly in water was approximately 20% of the fluid, when soaps prepared with 50% by weight of castor oil were used.

(b) Soaps prepared with 44% by weight of castor oil formed turbid fluids, but the fluids cleared on evaporating off the excess water. Very viscous fluids were formed when too much water had been evaporated off and part of the soap collected on the surface, as a skin, while hot.

(c) The fluids formed pink emulsions in water and 10% dilutions, prepared by standard method, did not show more than 3% cream separation after 24 or 48 hours. The fluids did not disperse rapidly, soda and potash soap fluids being about equal in this respect.

(d) The addition of 5% ethyl alcohol to a slightly turbid fluid made it quite clear and increased the rate of dispersion. It did not decrease the separation from a 10% dilution.

(e) The addition of 10% amyl alcohol to the same turbid fluid did not remove the turbidity but improved the rate of dispersion. The separation from a 10% dilution was unchanged.

(f) The addition of 5% benzene slightly improved the rate of dispersion without affecting the turbidity. The separation from a 10% dilution was increased by ½%, the equivalent of the benzene added.

The slight improvement in the rapidity of dispersion of the

fluid by the addition of ethyl alcohol, amyl alcohol, or benzene, was insufficient to warrant the addition; the experiments, however, suggested that a more aromatic hydrocarbon oil, e.g., coke-oven neutral oil, might be an improvement on the partly paraffinoid B.F. neutral oil. It was decided to experiment in this direction, a sample of coke-oven creosote oil being available.

Preparation of Coke-Oven Neutral Oil.

A sample of coke oven creosote oil (Wm. Baird & Co., Glasgow) was extracted at 50/60° C. with 9%-NaOH until the sodium hydroxide did not increase in volume. The extraction was completed with 18%-NaOH to remove the last traces of phenols, and the washed oil was cooled overnight in an ice chest to precipitate the naphthalene. The crude naphthalene separated by this means represented 12½% of the creosote oil. The physical constants of the oils were as follows:-

	C.O.Creosote Oil	C.O.Neutral Oil
Sp. Gr. 15.5°C	1.012	0.998
Tar Acids - 9% NaOH	17%	Nil
18% "		Nil
Yield of neutral oil		68.0%
" " crude naphthalene		12.5%
Distillation Test - 100 cc.		
I.P.	98°C	145°C
Water	0.6%	Trace

Dist. @ 190°C	8.0%	4.0%
200	24	10.0
210	40	18.5
220	52	29.0
230	63	39.0
240	70	52.0
250	76.5	63.5
260	81	72.0
280	86	81.0
300	90	86.5
320		92.0

Preparation of fluids by the addition of Sodium Castor-Oil Soap to mixtures of High Boiling Tar Acids and Coke-Oven Neutral Oil.

Fluids were prepared as previously described, by dissolving the soap in hot mixtures of the phenols and oil. The fluids prepared with coke oven neutral oil compared very favourably with the best commercial preparations and, on mixing with water, immediately formed white emulsions which were much thicker, or more opaque, than similar preparations with blast-furnace neutral oil. The emulsions did not cream to the top, as the specific gravity of the oil mixture was greater than that of water, but a deposit varying between ½% and 3% was obtained from 10% dilutions after settling. The measured amount deposited after 24 hours was not observed to increase, in four samples under test, when the period of settling was extended to seven days. These fluid preparations were so satisfactory that

quantitative work was commenced on the preparation of fluids containing varying proportions of the phenols and hydrocarbon oils, in order to determine the most efficient combination. Sodium castor-oil soap was employed since it was found to be quite as efficient as the potash soap and had the advantage of being the cheaper product. The following two soaps were prepared and used in the subsequent work.

Sodium Castor-Oil Soap No. 1
Castor oil = 46% on weight of finished soap

The castor oil was weighed into a bolt head flask, fitted with a mechanical stirrer and reflux condenser, and heated in a boiling water bath. The calculated weight of 8.37%-NaOH solution, equivalent to one-half of the quantity required to saponify the castor oil, was added and saponification afterwards completed by the addition of the necessary calculated weight of 17.12%-NaOH. The rate of addition of the sodium hydroxide solutions was regulated to prevent chilling of the soap mixture, and heating was continued until the oil was completely saponified. The soap was weighed finally and a small amount of water added to adjust to the calculated weight for a soap prepared with 46% by weight of castor oil. The soap set to a clear gel when cold and a sample was tested for free alkali and water.

Free Alkali:- A weighed quantity, about 3 gms., was dissolved in neutral alcohol and titrated with N/2-sulphuric acid using phenolphthalein as indicator. The pink colour of the alcoholic solution was discharged by 1 drop of the acid, which proved that the soap was neutral.

Water:- A weighed quantity of the soap, about 5 gms., was dissolved in the minimum amount of hot alcohol and the solution poured on to coarse dry sand in a deep petri dish, the weight of sand and petri dish being known. The alcohol was evaporated off slowly, the lumps of soap and sand broken down and the mixture dried at 105°C until constant in weight. The weight of the residual anhydrous soap and glycerine was subtracted from the weight of soap taken and the percentage of moisture calculated.

Water % - (1) 47.95 (2) 48.08 (3) 48.19 Mean - 48.10%

Sodium Castor-Oil Soap No. 2
Castor oil = 57% on weight of finished soap

The soap was prepared by the addition of the calculated equivalent amount of 17.12%-NaOH required to saponify the castor oil. The water bath temperature was raised to 105°C by the addition of common salt, in order to keep the soap sufficiently liquid for the working of the stirrer. The weight of soap was made up finally with water to give a finished soap prepared with 57% by weight of castor oil. The soap was clear at the finish of the saponification but became opaque when cold. The percentage free alkali and

water were determined as before.

Free alkali %	(1) 0.089	(2) 0.103	Mean = 0.1%
Water %	35.90	35.75	" =35.8%

The quantitative preparation of fluids with the above soaps was carried out in the following manner.

The volumes of high boiling tar acid and of coke-oven neutral oil were accurately measured from calibrated burettes, the rate of outflow being restricted to obtain perfect draining. The soap was weighed to within 0.05 grams of the required amount, as determined from previous qualitative tests. The minimum amount of soap was employed which would give perfectly formed emulsions, this amount increased as the percentage of high boiling tar acids in the fluids increased. The phenols, hydrocarbon oils and soap were mixed in an 8 oz. wide mouthed bottle, fitted with a mechanical stirrer and reflux condenser. The bottle was partly immersed in a water bath, which was then raised to the boil, and stirring was continued for ten minutes from the time the water commenced to boil. The fluid was cooled with constant stirring and transferred to a calibrated cylinder. The volume of the fluid was noted after draining, the temperature being adjusted to 15°C. Volume measurements were adopted for these fluids in preference to weighing, as all dilutions for the determination of the disinfectant value, or the size of the emulsion particles, were made by volume. The following fluids were prepared:-

Fluid A Oil phase - (25% H.B. tar acid by volume
(75% C.O. neutral oil "

A clear fluid was prepared with 80 c.c. of the above oil phase and 19.5 gms. of soap No. 1 (castor oil = 46% on weight of soap), the volume of the fluid was 98.0 c.c. This fluid did not separate on prolonged standing and formed a perfect white thick emulsion with water.

A deposit of soap was thrown down in a similar fluid to which 21.55 gms. of the same soap had been added. Further, a stable fluid could not be formed directly with this oil mixture and the more concentrated soap No. 2 (castor oil = 57% on weight of soap), the soap in this instance was thrown out on the surface of the oil but by the addition of water could be incorporated.

Fluid B Oil phase - (50% H.B. tar acid by volume
(50% C.O. neutral oil "

A clear stable fluid containing the minimum amount of soap was prepared by the addition of 17.5 gms. of soap No. 2 (castor oil = 57% on weight of soap) to 80 c.c. of this oil mixture, the volume of the fluid was 95.5 c.c. The emulsion given by the fluid in water was slightly pink in colour but thick and perfectly formed.

A turbid fluid, which emulsified perfectly in water, was formed by the addition of 24.65 gms. of soap No. 1 to 80 c.c. of the above oil phase. The cause of turbidity was found due to water and the fluid became clear when the

excess water was evaporated off. A clear fluid was obtained directly by the addition of 29 gms. of soap No. 1 to 80 c.c. of the above oil phase, but this fluid gave a thinner and more highly coloured emulsion than that containing 24.65 gms. of soap.

Fluid C Oil phase - (60% H.B. tar acid by volume
(20% C.O. neutral oil "

A satisfactory fluid was obtained with 80 c.c. of the above oil phase and 24 gms. of soap No. 2, the volume of the fluid was 101.8 c.c. An increase in the amount of soap changed the colour of the emulsion from a faint-pink to a brownish-fawn shade and decreased the opacity. The addition of soap No. 1 to the above oil phase gave fluids similar to those formed by the oil phase of fluid B.

Fluid D Oil phase - (H.B. tar acid alone.

A clear stable fluid, containing the minimum amount of soap, was prepared with 80 cc. H.B. tar acids and 32 gms. soap No. 2. The volume of the fluid was 109.1 c.c. The fluid formed a white emulsion with a slight fawn tinge and developed a pink colour on standing. An increase in the amount of soap changed the colour of the emulsion from white to brown.

Fluids in which the H.B. tar acids were present alone,

or were in excess of the oil, formed thinner or less opaque emulsions than those containing a greater proportion of oil. Table No. III summarises the preparation of fluids with the two sodium castor-oil soaps and, in addition, includes the 24-hour results of settling tests of 10% dilutions of the fluids in water and specific gravity determinations of the phenol-hydrocarbon oil mixtures, which form the oil phases of the fluids. The specific gravity of the oil phase increases from fluid A to fluid D and, as one would expect, the volume of the deposit which settles within 24 hours also increases in this order. It is observed, however, that increase in the proportion of soap decreases the tendency of the emulsions to settle, presumably by decreasing the particle size of the emulsions, but this addition of soap, which is in excess of the amount required for emulsification, spoils the appearance of the emulsions and increases the cost of the fluids. The particles which settle from emulsions prepared with the minimum amount of soap do not coalesce to form an oily layer but remain in the emulsified condition, and after several days may be redistributed in the emulsion by simple mixing. These observations led the writer to conclude that, for practical purposes, the more satisfactory comparison of the effect of the hydrocarbon oils on the phenols would be given by the fluids containing the minimum amount of soap required for emulsification.

TABLE III

No.of fluid	Constituents & Sp.gr. of oil phase	Soap No. 1		Soap No. 2
		Weight of castor-oil soap required to form		
		A clear fluid with excess soap (except A)	A turbid fluid but stable emulsion with minimum soap.	A clear fluid and stable emulsion with minimum soap
A	20 cc H.B.Ac. 60 cc C.O.Oil S.G. 1.005	20.3 gms (=15.6 gms No2) Diln.test 1%	-	No stable fluid formed
B	40 cc H.B.Ac. 40 cc C.O.Oil S.G. 1.013	29 gms (=22.3 gms No2) Diln.test 1%	23 gms	17.5 gms (=22.8 gms No.1) Diln,test = 2%
C	60 cc H.B.Ac. 20 cc C.O.Oil S.G. 1.022	50 gms (=38.5 gms No2) Diln.test 1%	32 gms Diln.test 3%	24 gms (=31.2 gms No.1) Diln.test = 3%
D	80 cc H.B.Ac. S.G. 1.032	49 gms (=37.7 gms No2) Diln.test 3%	37.5 gms Diln.test 7%	32 gms (=41.6 gms No.1) Diln.test = 4½%

The four fluids prepared with the minimum amount of soap and lettered A, B, C and D in Table III will be referred to again in the comparison of the emulsion particle size and disinfectant value. Several other fluids of similar type were prepared but their preparation presented no new distinctive features.

A number of unsuccessful attempts were made to prepare a fluid with C.O. neutral oil alone and castor-oil soap but the soap was thrown out of solution from the oil before a perfect emulsion was obtained. Riemann and van der Meulen (J.A.C.S., 1925, 47, 2511) say that "Phenol is a necessary

constituent of emulsions that can be prepared in the concentrated condition and diluted to give a milky emulsion with uniform globules". This statement confirms the writer's experience with the preparation of a fluid containing hydrocarbon oil and soap, but results later with rosin as the emulsifying agent have shown that the rosin acids may replace the phenol in this type of fluid.

Sodium Resinate as the Emulsifying Agent.

Sodium resinate was used in order to determine if it presented any distinctive features as an emulsifying agent and, particularly, to find if it could replace castor-oil soap, with any advantage. O.E. Ewe (J. Amer. Pharm. Assoc., 1920, 9, 47) recommends the use of rosin for the emulsification of substances immiscible with water and prepares a concentrated fluid by dissolving 40 gms. rosin in 100 gms. oil, with heat, and adding subsequently 20 gms. 25%-sodium hydroxide solution. The method was found suitable for the emulsification of pine oils heavily adulterated with kerosene and might, therefore, be applicable to hydrocarbon oils alone. The above proportion of sodium hydroxide is approximately 10% more than the theoretical amount required for complete saponification of the rosin.

A sample of commercial rosin, medium quality and brown in colour, was powdered and the saponification value determined. The results were:- (1) 160.5 (2) 160.3 (3) 160

Saponification value of rosin = 160.3

8 gms. rosin were dissolved in 20 gms. Coke-Oven Neutral Oil, by warming, and caustic soda solution was added until a stable emulsion formed. A very satisfactory thick emulsion was frequently obtained when about 65% of the equivalent amount of caustic soda solution had been added. The perfect emulsion stage was very transitory, however, and a lesser or greater amount of soda usually caused the separation of oil. The fluids, when cold, were seldom homogeneous owing to the separation of rosin or rosin soap. More consistent results were desired and rosin soaps were prepared which contained varying percentages of the equivalent amount of soda required for complete saponification. The only satisfactory results were obtained with the soap in which 65% of the rosin was neutralised. A stable fluid, which formed a very fine emulsion, was thus prepared and the proportions of the different constituents were 20 gms. C.O. neutral oil, 7.5 gms. rosin and 3.9 gms. 14%-sodium hydroxide solution. This result indicates that the free rosin is fulfilling the function of the phenols in the castor oil soap emulsions.

Rosin soaps did not give as good results as castor-oil

soaps for the emulsification of mixtures of coke-oven neutral oil and high boiling tar acids. The emulsions were much less opaque and, in contrast to the emulsification of C.O. neutral oil alone, it was found necessary to have about 10% more soda present than was required to neutralise the rosin. The amount of rosin increased as the percentage of H.B. Acid increased, e.g., 10 parts of rosin were required for the emulsification of 10 parts of H.B. tar acids and 30 parts C.O. neutral oil and 15 parts were necessary when the proportion of phenols to oil was 17.5 to 22.5.

PREPARATION OF STABLE EMULSION DISINFECTANTS

T H E O R Y

The technical method adopted for the preparation of stable emulsions and, according to Hatschek ("2nd Report on Colloid Chemistry" p. 19 H.M. Stat. Office, 1921), the probable process of formation of natural emulsions is that of the gradual addition of the disperse phase to the dispersion medium, during and continuous with the process of dispersion. K. L. Mark (J. Home Econ., 1921, 13, 477) emphasises the importance of this condition for the preparation of Mayonnaise and reports that, provided the olive oil is added to the egg yolk, or to the emulsion formed, within definite limits and the rate of addition does not exceed a certain maximum, then a stable emulsion always results.

Clayton ("Theory of Emulsions and Emulsification" 36, 1923) gives an example from the preparation of margarine where about 80% of oils are emulsified in 20% of an aqueous medium containing casein as the emulsifying agent. The oil-in-water emulsion is promoted by the slow addition of the oil to the water, and the water-in-oil type by the reverse process or by mixing the two constituents in bulk. The superior volume of the more abundant phase is therefore of importance but the phase-volume theory of Ostwald, which

postulated inversion of the type of emulsion when the volume concentration of the dispersed liquid exceeded 74% i.e. the calculated percentage for the closest packing of uniform spheres, is no longer tenable. Freundlich ("Colloid and Capillary Chemistry" trans. Hatfield, 1926, 833) mentions, however, that the critical ratio, 74.26, although not necessarily strictly adhered to, is usually satisfactorily fulfilled in emulsions with even sized particles and thin protective envelopes.

Cooper (Biochem J., 1912, 6, 362) found that gelatine was soluble in warm anhydrous phenol and in m-cresol, and could be recovered unaltered from the solutions by dialysis. The solubility of gelatine in cresol is of importance when its use is contemplated for the emulsification of cresol and its homologues in water, as the partition of the gelatine between the cresol and water will vary with the volume concentration of the phases and influence the type of emulsion. Woodman (J. Phys. Chem. 1926, 30, 658/672) studied the system cresylic acid-gelatine-water and found that both types of emulsions were formed, excess of one liquid phase determined the type formed and this liquid became the external phase. The water-in-cresylic acid type of emulsion was usually the more stable. Where the phases were present in equal proportion and both types of emulsions seemingly possible, the water-in-cresylic acid type was formed with fresh gelatine

solutions, but with old gelatine solutions a stable cresylic acid-in-water emulsion was produced. Woodman suggested that the new gelatine solutions were emulsoid, while the old solutions had a solid network structure and contained debris not so readily dissolved by the cresylic acid. Heating old gelatine solutions was found to reverse the ageing process and, concordant with this result, a higher temperature made emulsification more difficult.

It is known that the stability of colloids depends largely on the charge of the colloid particle and increasing the charge on many emulsions has been found to have a stabilising effect. Oil-in-water emulsions are, in general, negatively charged and salts like NaCl, KCl, Na citrate, NaOH, and Na_2HPO_4 (Ghosh and Dhar, J. Phys. Chem. 1926, 30, 294; Bhatnagar, J.C.S. 1920, 117, 542; 1921, 119, 61, 1760) favour the formation of these emulsions. The effectiveness of the salts is determined by the adsorption of the anion by the oil globule and consequent increase in the negative charge, but an excessive amount of the electrolyte will cause separation or inversion of the emulsion. With emulsoid sols the charge and protective action are dependent upon the pH value. The emulsoid sols change their charge under the influence of the hydrogen-ion concentration of the medium i.e. they become positively charged in an acid solution and negatively charged in a basic solution (Kruyt

and Klooster "Colloids" 1927, 88). The effect of this change of charge is evident in the action of gelatine on a negatively charged gold sol, as the sol is protected by neutral and gelatinate ions but precipitated by cationic gelatine hydrochloride (Rideal, Proc. Camb. Phil. Soc., 1923/25, 22, 101).

The use of sodium hydroxide as a stabiliser for tar acid-gelatine-water emulsions seems to present several distinct advantages. The phenols are acidic and the neutralisation of this acidity should increase the negative charge on the oil globules and improve the stability of the gelatine by raising the pH value above that of its iso-electric point, viz., pH 4.7. A maximum pH value is to be expected as Kruyt and Klooster (ibid 196) show that the viscosity of gelatine, which is dependent on the electric charge, increases to a maximum on either side of the iso-electric point and then decreases. Holmes and Childs (J.A.C.S., 1920, 42, 2049) studied the emulsification of kerosene in water by the aid of gelatine and found viscosity to be the leading factor. The best viscosity was much greater than that of water and this result was better attained by the use of a larger amount of gelatine, liquefied by the proper electrolytes, than by only a small amount of the emulsifying agent.

A satisfactory laboratory method of emulsification

was sought, which would compare with technical methods of emulsion preparation, and it was decided that Hatschek's emulsifier (cf Holmes "Laboratory Manual of Colloid Chemistry" N.Y., 1922, 57) was suitable, although a possible disadvantage of air stirring was the demulsification by air bubbles. Nugent (Trans. Far. Soc., 1921, 17, 703) found the demulsification of benzene-gelatine emulsions on rotation in tubes to be proportional to the air space. The emulsions prepared by the Hatschek apparatus were improved by homogenisation in the manner described by Briggs (J. Phys. Chem., 1915, 19, 223) but with reduced pressure in the emulsion receiver. Stamm ("Colloid Symposium Monograph" II, N.Y., 1925, 70) found that a benzene-in-water emulsion, stabilised by gelatine, was completely broken by a single homogenisation and, with atmospheric pressure in the receiver, homogenisation tended to break all the emulsions studied. Homogenisation, however, with low pressure in the receiver increased the degree of dispersion of benzene-in-water emulsions stabilised with soap.

EXPERIMENTAL

Selection of Emulsifying Agent.

Experiments with gelatine as the emulsifying agent were unsatisfactory and all attempts to prepare stable oil-in-water emulsions containing 50% of high boiling tar acids were unsuccessful, even with the addition of sodium hydroxide

or sodium phosphate as the stabilising agents. Skin glues gave similar results to gelatine. Bone glues, however, gave satisfactory results and 60% of H.B. tar acids could be readily emulsified. Inversion of the emulsion from oil-in-water to water-in-oil occurred when the volume concentration of the oil phase reached 70%, or thereabout.

Preparation of Glue Emulsions with a "Hatschek" Emulsifier.

The sample of bone glue employed in the following experiments, known commercially as a No. 1 filtered bone glue, was obtained from David Forrest & Sons, Paisley. The moisture, ash and non-gelatinous substances were determined by the methods given in "Allen's Commercial Organic Analysis" 1914, 8, 612.

Moisture %	13.9%
Ash %	1.32%
Non-gelatinous substances %	12.4%

Emulsions containing 1%, or less, bone glue were unstable compared with emulsions containing higher percentages of glue. It was decided to use 2½% glue in the emulsions and experiments were made to determine the effect of temperature, sodium hydroxide, sodium chloride, sodium phosphate and hydrocarbon oil on the efficiency of emulsification. The glue, 2½ gms, was immersed overnight in water then dissolved by raising the temperature to that at which the emulsification was conducted. Sodium hydroxide or other

salts were now added, the weight made up to 50 gms. and the solution transferred to the cylinder of the Hatschek apparatus, shown in sketch, Fig. I (p.51a). The high boiling tar acids, 50 gms, were run slowly into the open thistle funnel, the rate of flow being adjusted so that the time taken was 40 to 45 minutes.

Table IV. gives several preparations made by this method. The cream separated from the emulsion refers to the bottom layer, as the specific gravity of the oil phase was greater than unity and the emulsion particles settled downwards. The results of settling tests on 10% dilutions of the emulsions are included.

The following conclusions were arrived at from the preparation of glue emulsions with the Hatschek emulsifier.

(1) The emulsions were unstable in the sense that all creamed in the concentrated emulsion condition and the emulsion particles completely settled from 10% dilutions in water, after standing for periods of three days or more.

(2) An increase in temperature from 50°C to 75°C assisted emulsification.

(3) The addition of Sodium Hydroxide decidedly improved the appearance and stability of the emulsions. The amount of N/1-NaOH must not exceed 5% of the finished emulsion.

(4) The addition of coke-oven neutral oil to the phenols improved the appearance and stability of the emulsions. Inversion of the emulsion resulted when the proportion of the hydrocarbons to the phenols reached 40%

(5) The addition of small amounts of sodium chloride or sodium phosphate in conjunction with sodium hydroxide was more effective than increasing the sodium hydroxide alone.

TABLE IV

Emulsions prepared with Hatschek's emulsifier and containing 50% high boiling tar acids and 2½% bone glue as emulsifying agent.

No.	Temp. °C.	Additional materials	Appearance of Emulsion after		%ge settled from 10% dilutions after			
			4 days	30 days	3hrs	5hrs	24hrs	72hrs
1	100	None	No cream	80% cream C.	1	2	6	7
2	75	"	80% "	--- H	4	-	6	C
3	55/60	"	50% "	50% " C.	4	5	6	C
4	"	1.0cc N/1 NaOH	Improved	66% "	1	1½	5	7
5	"	1.25 "	80% cream	--- H	1	3	5	7
6	"	2.50 "	88% "	--- H	½	1	4½	6
7	"	5.0 "	60% "	60% " C.	1½	2½	5	6
8	75	5.0 "	Improved	60% " C.	1¼	1¾	4¾	6
9	"	10.0 "	50% cream C.	Broken	4	4½	5½	C
10	"	2.50cc " 0.1 gms NaCl	60% "	50% cream C.	-	-	3½	5½
11	"	2.5cc N/1-NaOH 0.025 g. NaCl	60% "	--- H	½	1½	4½	5½
12	"	0.1 g. Na_2HPO_4	60% "	50% " C.	-	-	5	6
13	"	1.25cc N/1 NaOH 0.01 g Na_2HPO_4	66% "	60% "	-	¼	2	4
14	"	2.5cc N/1-NaOH 2.5 gms C.0.0il (47.5g.H.B.Acid)	75% "	H	¼	½	3	5
15	"	2.5cc N/1-NaOH 7.5gms C.0.0il (42.5g.H.B.Acid)	No cream	80% "	Trace	-	1½	3½
16	"	2.5cc N/1-NaOH 18.0gms C.0.0il (32.0g.H.B.Acid)	No cream Mottled appearance	Emulsion inverted to W-in-O.	Nil	—	1	3

C - Emulsion particles coalescing together to form a liquid layer.
H - These emulsions were used in homogenisation experiments.

Homogenisation of Glue Emulsions.

A number of the emulsions prepared with the Hatschek emulsifier were homogenised in a simple Brigg's homogeniser. The homogeniser consisted of two 200 cc. wide mouthed bottles which were fitted with the arrangement of corks and tubes shown in sketch, Fig. II (p.51a). The emulsion was drawn from A into B and vice versa, by interchanging the stoppers. The emulsion entered B through inlet tube C, which was drawn out to a capillary $\frac{1}{2}$ to 1 mm. in diameter, and impinged against the side of the bottle which was about 2 mm. distant. Better homogenisation of the emulsions was obtained at high than at low temperatures, and a temperature of 75° C. was chosen. The following settling test results were given by 10% dilutions of emulsions prepared by the Hatschek emulsifier and passed 10 times through the homogeniser. The numbers refer to the preparations in Table IV.

TABLE V.

No.	Percentage settled from 10% dilutions of emulsions after					
	1 day	2 days	3 days	5 days	7 days	11 days
2	2	$3\frac{1}{4}$	—	6	—	—
5	$1\frac{1}{4}$	2	3	4	$4\frac{3}{4}$	$5\frac{1}{2}$
6	1	-	-	$4\frac{1}{4}$	-	$5\frac{1}{2}$
11	$\frac{1}{2}$	1	$1\frac{1}{2}$	$2\frac{1}{4}$	3	$4\frac{1}{2}$
14	$\frac{1}{2}$	1	$1\frac{1}{2}$	$2\frac{1}{4}$	3	$4\frac{3}{4}$

The above homogenised emulsions, with the exception

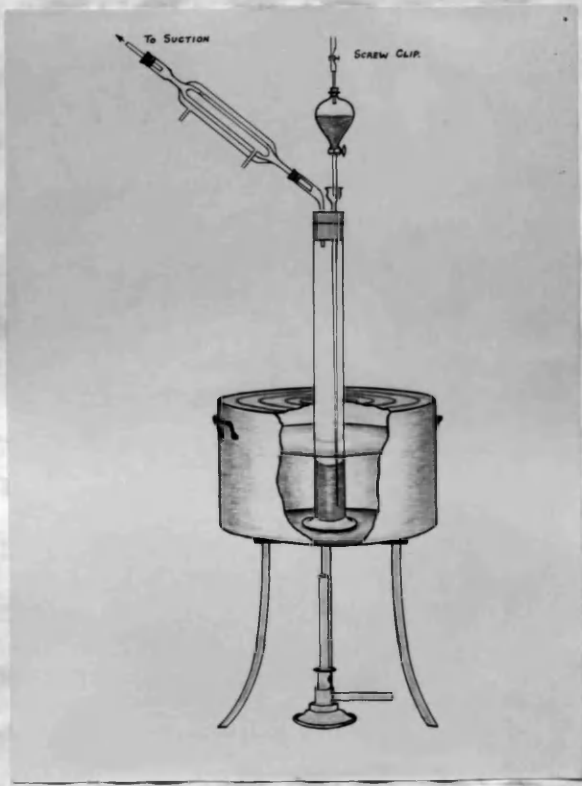


Fig. I

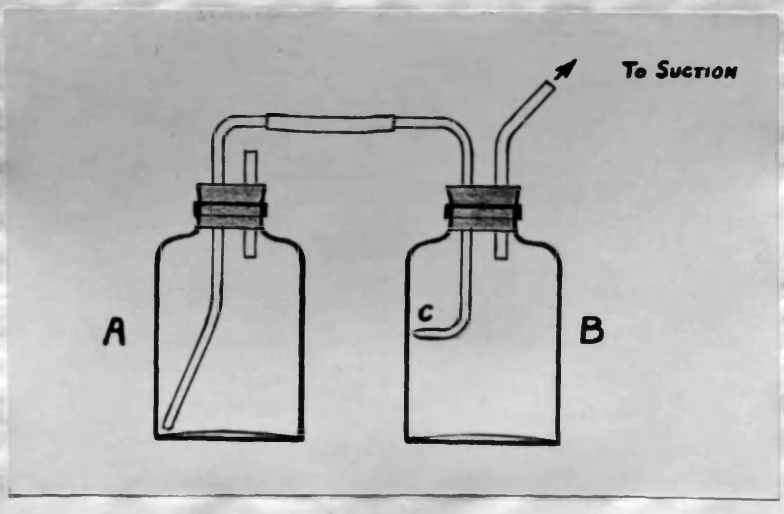


Fig. II

of number 2, did not cream like the Hatschek emulsions and form two distinct layers, but the large particles slowly settled to the bottom. The results show that these emulsions can be effectively homogenised and a "Hunter" Emulsor, which was kindly given by the makers, was next employed to further increase the dispersion.

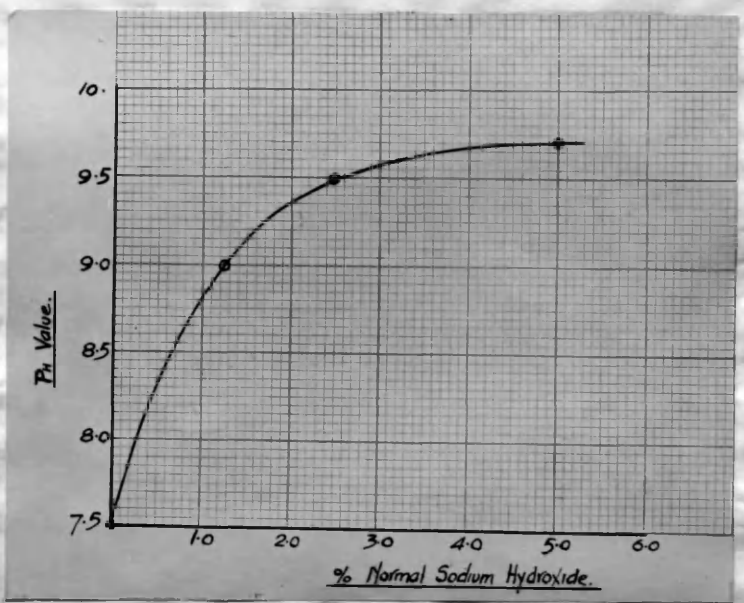
Action of Sodium Hydroxide on Glue Emulsions.

Before preparing emulsions with the "Hunter" machine, which meant preparing not less than one litre, it was decided to investigate the action of the sodium hydroxide.

Nugent (Trans. Far. Soc., 1921, 17, 703) found that sodium hydroxide destroyed the protective action of gelatine and, in the present investigation, the emulsifying power of the glue was found to be seriously impaired by immersion in water containing 2% N/1-NaOH for 24 hours, followed by solution at 75°C. The sodium hydroxide appears to react with the phenolic bodies which, being only weakly acidic, may act in the manner of buffer salts. The pH values of several of the emulsions prepared by the Hatschek emulsifier were determined by the electrometric method, in order to verify this hypothesis, and the results are reported in tabular and graphical form.

TABLE VI.

No. of Emulsion	Added Electrolyte	pH Value of emulsion
1	None	7.5
5	1.25% N/1-NaOH	9.0
6	2.50% "	9.5
7	5.0% "	9.7
12	0.10% Na_2HPO_4	7.9



The results show that the phenols have a decided buffering action and that no advantage will be gained by increasing the N/1-NaOH concentration beyond 2.5%.

Preparation of Emulsions with a "Hunter" Emulsor.

The "Hunter" Emulsor consists essentially of two intermeshing pinion wheels which revolve inside a closely fitting figure eight seating. The right-hand pinion wheel is

directly coupled to an electric motor which is rotating at 3,000 revolutions per minute. The emulsion flows from the lower of two conical containers into the top centre of the pinion wheel casing, which is mounted vertically, is carried round the inside of the casing in the "V" shaped cavities formed between consecutive teeth and the casing and is ejected from the bottom of the pinion wheel casing through a pipe which connects with an upper conical container. The upper container is mounted directly above the lower container and a valve at the outlet of the upper container, when open, permits of continuous circulation of the emulsion. Emulsification is primarily produced by the intensive mixing which is given the liquids within the pinion wheel casing. Homogenisation can only be obtained by repeated circulation of the emulsion.

Several emulsions were prepared in order to determine the effect of varying the time of addition of the phenols to the glue solution. The machine was not fitted with a water-jacket and was heated by circulating boiling water through it previous to use. The following quantities of the constituents of the emulsion were added in each case.

Bone Glue	25 gms.
Water	475 cc
N/1-NaOH	12.5 cc
H.B. Tar Acids	500 gms

The glue was immersed overnight in water and brought into

solution by heating to 100°C. The hot glue solution was poured into the emulsifying machine and circulation immediately commenced. The N/1-NaOH was added and the H.B. tar acids, which had been heated to 100°C, were run into the lower container at a predetermined rate from a graduated separator. The following are details of three experiments:-

(1) In this instance the phenols were added to the glue solution in 1½ minutes and circulation was continued for a further 8½ minutes. The temperature of the emulsion at the end of the ten minutes circulation was 46°C. A stable viscous water-in-oil emulsion was obtained.

(2) The time taken to add the phenols was increased to 5½ minutes, the initial rate being 100 cc. per minute. The total time of emulsification was ten minutes, as before, and the final temperature of the emulsion was 44°C. A fawn coloured oil-in-water emulsion was obtained which showed no sign of separation one week later and only 1% settled from a 10% dilution after 7 days. Four months later a 25% cream had settled to the bottom but the emulsion particles had not coalesced together to form oil globules.

(3) The phenols were added to the glue solution at a slower and constantly decreasing rate. The rates of addition and temperatures of the emulsion were as follows:-

Rate	Time	Amount added	Temperature
28 cc. per min.	5 mins.	140 cc	-
22 "	10 "	250 "	43°C
18 "	15 "	340 "	40 "
16 "	20 "	420 "	38 "
12 "	25 "	480 "	37 "
8 "	27½ "	-	37 "

The total time of emulsification was 30 minutes. A fawn coloured oil-in-water emulsion was obtained. The settling test of a 10% dilution and the cream separation in the concentrated emulsion, after four months' settling, were exactly the same as in No. 2 emulsion. Results on the particle size and germicidal value of this emulsion are given later, in comparison with Hatschek and Hatschek homogenised emulsions.

These results show that the production of an oil-in-water emulsion, containing phenols emulsified in glue solution, is dependent upon the rate of addition of the phenols, as too rapid addition causes the formation of a water-in-oil emulsion. The similarity in the stability and dilution settling tests of emulsions numbers 2 and 3 indicates that a longer time of attrition in the Hunter machine has had little effect upon the emulsion. The stability of these emulsions, however, is not entirely dependent upon homogenisation, as experience has shown that the nature of the phenols and of the glue has a greater effect in the production of a stable emulsion than homogenisation.

DETERMINATION OF THE PHENOL COEFFICIENT VALUES OF DISINFECTANT FLUIDS AND EMULSIONS

Method of Test.

The disinfectant values of the fluids and emulsions were determined by the Rideal-Walker method, according to the revised technique in the authors' brochure entitled "Approved Technique of the Rideal-Walker Test" and published by H. K. Lewis & Co., Ltd., in 1921. The disinfectant values were found to vary markedly with slight variations in the acidity of the culture broth, but this effect will be particularly referred to later and it will suffice to say that the phenol coefficients reported in this section were obtained with a pH 7.3 broth.

Preparation of Pure Phenol Solution.

The purity of the phenol employed as the control in the Rideal-Walker test has received attention from Walker & Weiss (M.O., 12th May, 1923) and they have recommended that only pure phenol, M.P. 40.5°C, should be employed and the melting point determined on a 50 cc sample. Phenol of this standard of purity was obtained in the middle fraction, representing 60% of the charge, from the vacuum distillation of a sample of Phenol M.P. 40°C. A stock 5% solution of the pure phenol was prepared and checked by titration with bromine. The two methods for the estimation of phenol which

are outlined by Spielmann ("The Constituents of Coal Tar" London, 1924, 117) were less satisfactory than the direct titration method of Callan & Henderson (J.S.C.I., 1922, 41, 1617). The method was modified to suit the standardisation of the phenol solution, as follows:- To 50 cc of a 0.1% solution, which was prepared by accurate dilution of the 5% solution, were added 3 gms potassium bromide and 5 cc concentrated hydrochloric acid. The mixture was titrated with N/10-bromate solution (2.784 gms $KBrO_4$ and 10 gms KBr per litre) with constant shaking until a slight excess of free bromine, about 1 cc, was present and coloured the solution faintly yellow. 5 cc 5% potassium iodide solution and 1 cc starch solution were now added and the liberated iodine, equivalent to the excess bromine, titrated with N/10-sodium thiosulphate solution. A sharp end-point was obtained and the precipitated tribromophenol was not tinted blue by the starch and iodine.

Preparation of Disinfectant Dilutions.

A consistent method of preparing emulsions from the disinfectant fluids was desired, as it was considered that the rate of addition of the fluid to water and the amount of agitation would influence the degree of dispersion. A suitable method appeared to be the regulated addition of the fluid to water, while being stirred at constant speed. Excellent results were obtained with fluid A but the method

was found inapplicable to fluids B and C, as imperfect emulsions containing visible oil globules were obtained. The method was not made practicable by reducing the speed of stirring, or by increasing the proportion of soap in the fluids. Fluids B and C, it was observed, did not disperse quickly when added to still water, part of the fluid always settling on the bottom of the vessel in an unchanged condition. The settled material dispersed readily, however, a few minutes later when the vessel was gently rotated, and subsequently the emulsion did not break down on agitation on a shaking machine for two hours. The reason for the difference between this method of dilution and the stirring method depends apparently upon two factors, viz., the rate of solution of the soap and the rate of adsorption of the soap by the oil phase. By the stirring method the rate of solution of the soap is probably greater than the rate of adsorption by the oil phase, if so the oil globules will be imperfectly protected and immediately coalesce together.

The following method was adopted, for the preparation of disinfectant fluid dilutions:-

5 cc of the fluid were measured in a dry sterile pipette, calibrated to contain this quantity, the outside of the pipette was wiped dry with sterile gauze, and the contents were delivered into a 250 cc bottle which contained 195 cc of sterile distilled water. The pipette was washed out into the emulsion, and a preliminary mix given by gentle

rotation of the bottle. The bottle was agitated on a shaking machine, oscillating 260 times per minute, for 15 minutes, in order to obtain uniform mixing. The time period of agitation was arbitrary, as special tests with soap fluid emulsions had shown that shaking for 1 minute or for 1 hour did not alter the coefficient value. An aliquot portion of the 2½% emulsion, immediately after agitation, was diluted to form a ½% or 1% emulsion, depending on the disinfectant value of the fluid. The ½% or 1% emulsion was used for the preparation of all higher dilutions.

The dilutions of the glue emulsions were made without mechanical agitation, as these fluids were already in the emulsified form. The shaking of 2½% dilutions of the glue emulsions for an equal time period to the soap emulsions caused a number of the emulsified particles to coalesce together and form visible oil globules. The extent to which these emulsions are broken by agitation may be a measure of their stability, as the effect of agitation was less apparent when the glue emulsions were most stable.

Rideal-Walker Phenol Coefficient Values of Castor-Oil Soap Fluid Disinfectants.

The sodium castor-oil soap fluids, containing varying proportions of high boiling tar acids and coke-oven neutral oil, were first tested in order to determine the best proportions to employ. The preparation of the fluids was given on pages 36 and 37. The phenol coefficients were

determined by the R. W. method, under the following conditions:-

Temperature of medication, 17/18°C

Culture, B. Typhosus (Lister) - 5th day's 24 hour broth subculture. Broth pH 7.3

Proportion of culture to disinfectant, 0.5 cc to 5 cc

Period of incubation, 48 hours. Temperature, 37°C

Two typical charts for each of the fluids A, B, C and D, are given in Table VII with the total number of tests and average phenol coefficients.

The effect of the increase in the proportion of H.B. Tar acids in the fluids is more readily observed in Table VIII. The constituents of the fluids are expressed as volume percentages, the volume of the anhydrous soap being the difference between 100% and the sum of the other constituents. Column No. 5 shows that the germicidal efficiency of the fluids increases to a maximum value with fluid C, containing approximately 60% of H.B. tar acids. Column No. 6 expresses this germicidal action as a function of the phenol-hydrocarbon oil mixture, and the maximum is again reached with fluid C. If the phenols are regarded as the only germicidal agent in the disinfectant fluids, then the figures in column 7 show that they are employed to greater advantage in fluid A than in any of the other fluids and this result might be explained by a decrease in the

TABLE VII

Date	Disinfectant	Dilutions	Time in contact with disinfectant, minutes				No. of Tests	Average phenol coeff.
			2½	5	7½	10		
26/2/26	Fluid A	1:1100	X	-	-	-	4	12
	"	1:1200	X	X	-	-		
	"	1:1300	X	X	X	-		
	"	1:1400	X	X	X	X		
	Phenol	1:100	X	X	-	-		
12/3/26	Fluid A	1:1100	X	-	-	-		
	"	1:1200	X	-	-	-		
	"	1:1300	X	X	-	-		
	Phenol	1:100	X	-	-	-		
	"	1:105	X	X	-	-		
25/1/26	Fluid B	1:1800	X	-	-	-	3	20
	"	1:1900	X	X	-	-		
	"	1:2000	X	X	-	-		
	"	1:2100	X	X	X	-		
	Phenol	1:100	X	X	-	-		
2/2/26	Fluid B	1:2000	X	X	-	-		
	"	1:2100	X	X	X	-		
	"	1:2200	X	X	X	X		
	Phenol	1:100	X	X	-	-		
	"	1:105	X	X	X	-		
5/2/26	Fluid C	1:2000	X	-	-	-	4	22
	"	1:2200	X	X	-	-		
	"	1:2400	X	X	X	-		
	"	1:2600	X	X	X	X		
	Phenol	1:100	X	X	-	-		

TABLE VII (Contd.)

9/2/26	Fluid C	1:2000	X	-	-	-	4	22
	"	1:2200	X	X	-	-		
	"	1:2400	X	X	X	-		
	"	1:2600	X	X	X	X		
	Phenol	1:100	X	X	X	-		
19/2/26	Fluid D	1:1800	X	X	-	-	3	18
	"	1:2000	X	X	X	X		
	"	1:2200	X	X	X	X		
	"	1:2400	X	X	X	X		
	Phenol	1:100	X	X	-	-		
9/3/26	Fluid D	1:1800	X	X	-	-		
	"	1:1900	X	X	X	-		
	"	1:2000	X	X	X	-		
	"	1:2100	X	X	X	X		
	Phenol	1:100	X	X	-	-		

TABLE VIII

Fluid	(1) H.B.Tar Acids Vol. %	(2) C.O.N. oil Vol.%	(3) Water in soap Vol %	(4) Anhyd. soap Diffce.	(5) R.W. phenol coeff.	(6) Coeff x 100 / % Acids & Oil	(7) Coeff x 100 / % Acids
A	20.4	61.2	9.6	8.8	12	14.7	58.8
B	41.9	41.9	6.3	9.9	20	23.9	47.7
C	58.9	19.7	8.7	12.7	22	28.0	37.3
D	73.3	-	10.8	15.9	18	24.6	24.6

emulsion particle size, which is promoted by the greater excess of hydrocarbon oil present. The presumption that the soap and coke-oven neutral oil have no disinfectant value must, however, be proved.

Disinfectant value of Soap and Neutral Oil.

A 20% solution of sodium castor-oil soap (castor oil = 57% on weight of soap) was prepared in distilled water and the disinfectant value tested by the Rideal-Walker method. No disinfecting action was observed in this or weaker dilutions and the result shows that the soap alone has little germicidal action, within the time of contact obtaining in the test.

In order to test the action of the coke-oven neutral oil it was necessary to emulsify it. The Hatschek emulsifier described previously was used and 40 gms. of oil were slowly added to a solution of 10 gms of soap in 50 gms water. A second emulsion was prepared under the same conditions with C.O. neutral oil which had been washed free from basic bodies. The bases were removed by washing with sulphuric acid (S.G. 1.25) and the oil was afterwards sprayed with water then washed with sodium hydroxide (S.G. 1.1). The dehydrated crude pyridine represented 6.3% of the oil.

Both emulsions were a light brown colour and creamed completely on standing, the rate of creaming being slightly more rapid with the washed oil. The disinfectant values of

the emulsions were:-

R.W. phenol coeff. of C.O. neutral oil emulsion = 1.0
" " " acid washed " " " = 0.6

The neutral oil therefore has a decided germicidal action which is not attributable to bases alone, but this germicidal action is small in comparison with that of the high boiling tar acids. The reduction in the coefficient value of the acid washed neutral oil cannot be entirely attributed to pyridine, as Kingzett and Woodcot (Analyst, 1913, 38, 190) report that the R.W. phenol coefficient of commercial pyridine is only 0.38. It would appear, therefore, that the action of the combined bases and hydrocarbon oils is connected with the ease and degree of emulsification, in a similar manner to the phenols and hydro-carbon oils.

Rideal-Walker Phenol Coefficient Values of additional Soap-Fluid Disinfectants.

The results in Table VIII show that the highest phenol coefficient per unit of Tar Acid present is obtained with the fluid containing 20% tar acids, and further tests were made to determine if this high value was obtained with fluids containing 30% to 35% H.B. tar acids and emulsified with sodium or potassium castor-oil soaps.

Fluid E - Preparation and Disinfectant Value.

30 cc H.B. tar acids	=	29.1%	by volume
50 cc C.O. neutral oil	=	48.5%	" "
25 gms. sodium castor oil	=	10.8%	" " soap
soap - 48.1% water	-	11.6%	" " water

Volume of fluid - 103 cc.

Rideal-Walker tests.

8/3/26	Fluid E	1:1700	X	X	-	-	12/3/26	X	-	-	-
	"	1:1800	X	X	X	-		X	X	-	-
	"	1:1900	X	X	X	-		X	X	X	-
	Phenol	1:100	X	X	-	-		X	-	-	-
		1:105	X	X	X	-		X	X	-	-

R.W. phenol coefficient = 17 (Average of 3 tests)

(Coeff. x 100) ÷ (% Acids & Oil) = 21.9
(Coeff. x 100) ÷ (% Acids) = 58.4

This result proves that the high germicidal efficiency, relative to the phenol content, is maintained with phenols containing 30% of high boiling tar acids.

Fluids containing 35% H.B. Tar Acids

The fluids were prepared by weight and the soaps used were neutral and contained 57% by weight of castor oil, or oleic acid.

	Sodium castor-oil soap fluid.		Potassium castor oil soap fluid	
	Wt%	Vol. %	Wt.%	Vol. %
H.B. tar acids	35	34.70	35	34.8
C.O. neutral oil	45	46.1	45	46.2
Soap	20	19.2	20	19.0
Density	1.0193		1.0226	

Rideal-Walker Tests.

1-3-27	Fluid	1:1800	X	X	-	-		X	X	-	-
	"	1:2000	X	X	X	-		X	X	X	X
	"	1:2200	X	X	X	X		X	X	X	X
	Phenol	1:95	X	X	X	-		X	X	-	-
	"	1:100	X	X	X	X		X	X	X	X
2-3-27	Fluid	1:1700	x	x	-	-		x	-	x	-
	"	1:1800	x	x	-	-		x	x	-	-
	"	1:1900	x	x	x	-		x	x	x	-
	"	1:2000	x	x	x	x		x	x	x	-
	Phenol	1:95	x	x	-	-		x	x	-	-

R.W. phenol coefficient = 19
Do. per unit H.B. acid & oil = 19 ÷ 0.808 = 23.5
Do. " " H.B. acid only = 19 ÷ 0.347 = 54.7

Castor-oil soap fluids containing 35% by weight of H.B. tar acids show a slightly reduced germicidal efficiency, relative to the tar acid content, compared with fluids containing less H.B. tar acids. Tait (J.S.C.I., 1926, 45, 416T) recommends the employment of potash castor-oil soap for fluids of highest coefficient value and gives the following approximate coefficient values for fluids containing varying proportions of high boiling tar acids:-

35% high boiling tar acids	Coefficient	20	and over
25% " " " "	"	15	" "
20% " " " "	"	10	" "

The employment of potash soaps in preference to sodium soaps has not been found by the writer to improve the disinfectant value of the fluids. The following tests with sodium and potassium oleate soap fluids, prepared similarly to the previous castor-oil soap fluids, supply confirmation of this statement.

Rideal-Walker Tests.

Fluid dilution	Sodium Oleate	Potassium Oleate
1:300	- - - -	- - - -
1:600	x - - -	x - - -
1:900	x x - -	x x - -
1:1200	x x x -	x x x x
Phenol dilution 1:100	x x - -	x x - -

R.W. phenol coefficient (approximately) = 9

This result shows that the oleate soap fluids have only about

one half the germicidal value of similarly prepared castor oil soap fluids.

A similar serious reduction in the disinfectant value of the fluid is observed if, instead of a change in soap, the coke-oven neutral oil is replaced by blast-furnace neutral oil. A fluid was prepared containing by weight:- 35% H.B. tar acids, 45% B.F. neutral oil and 20% sodium castor oil soap. The results for this fluid are compared below with those of similarly prepared fluids containing coke oven neutral oil, the oil in one preparation having been washed free from pyridine bases. The acidity of the Rideal-Walker broth with which the tests were conducted was pH 7.6 in this case.

Blast Furnace Neutral Oil Fluid:

			(1)				(2)			
20/5/27	Fluid dilutions	1:800	x	x	-	-	x	-	-	-
		1:900	x	x	x	-	x	x	-	-
		1:1000	x	x	x	x	x	x	x	-
		1:1100	x	x	x	x	x	x	x	x
	Phenol dilution	1:100	x	x	-	-	x	x	-	-

R.W. phenol coefficient = 8.0 9.0
= (Mean) 8.5

Coke-Oven Neutral Oil Fluids

		C.O.Neutral oil contg. bases				C.O.neutral oil free from bases			
29/6/27 Fluid dilution	1:1800					x	-	-	-
	1:2000	x	x	-	-	x	x	-	-
	1:2200	x	x	x	x	x	x	-	-
	1:2400	x	x	x	x	x	x	x	x
Phenol "	1:95	x	x	-	-	x	x	=	=
	1:100	x	x	x	-				

R.W. phenol coefficient = 21 21/23

The results prove that the high disinfectant value of fluids prepared with coke-oven neutral oil is not due to the pyridine bases present in the ordinary oil and the nature of the hydrocarbons must be principally responsible.

The influence of emulsion particle size on the disinfectant value of these fluids will be discussed more fully in conjunction with particle size determinations, but it was necessary to obtain the phenol coefficient values at this stage for comparison purposes later. The phenol coefficient values of these soap fluid disinfectants are not dependent entirely upon the H.B. tar acids present and, therefore, no direct comparison can be obtained between the germicidal power of the phenols and the emulsion particle size. In order to have this data, however, glue emulsions with H.B. tar acids alone were prepared and tested, as follows.

GLUE EMULSION DISINFECTANTS

Hatschek Emulsion.

50 gms high boiling tar acids were emulsified in 50 gms. glue solution containing 2½ gms. Bone Glue and 1.25 cc N/1 NaOH, with the aid of the Hatschek apparatus previously described. The temperature during emulsification was 75°C and the time of adding the acid was 45 minutes. The preparation was repeated and the two emulsions mixed. Owing to the apparatus being washed out with water at the

finish, the percentage of H.B. tar acids in the emulsion was 48.7% by weight.

Hatschek Homogenised Emulsion.

One half of the Hatschek emulsion was homogenised 10 times at 75°C in the Brigg's homogeniser. The emulsion lost weight owing to the evaporation of water and the percentage of H.B. tar acids was increased to 52%. This loss in weight was not made up, as it was decided to control the percentage phenols present by decomposing the emulsion.

Hunter Emulsion.

The preparation of this emulsion is given on page 55 (No. 3). The percentage of phenols in this emulsion had to be determined by decomposition, as the machine retained a proportion of the emulsion and the loss by evaporation was about 5%.

Determination of Percentage Phenols Present.

The method recommended in Allen's "Commercial Organic Analysis" was followed, and the emulsion decomposed with hydrochloric acid then extracted with ether. 50 cc of the emulsions were boiled for 5 minutes under a reflux condenser with 10 cc of concentrated hydrochloric acid. The decomposed emulsion was cooled then extracted with three separate 50 cc portions of methylated ether, and the combined ether extracts dried over anhydrous sodium sulphate. The ether

was distilled off from a weighed Wurtz flask and the flask dried in a steam oven until constant in weight. The results obtained for the percentage of phenols in the emulsions were:-

% phenols in Hatschek emulsion	45.6% by volume		
% " " Hatschek homogenised em.	48.7% " "		
% " " Hunter emulsion	(1)49.8%	(2) 50.0%	

The results, although comparative between themselves, are low but material did not permit repeating the extraction by other methods.

Rideal-Walker Phenol Coefficient Values of Glue-Emulsion Disinfectants.

Hatschek Emulsion

16/11/26	Emulsion dilution	1:1300	x	x	-	-	25/2/27	x	x	x -
		1:1400	x	x	x	-		x	x	x x
		1:1500	x	x	x	x		x	x	x x
		1:1600	x	x	x	x		x	x	x x
	Phenol dilution	1:95	x	x	-	-		x	x	x -
		1:100						x	x	x x

R.W. phenol coefficient = $\frac{1300}{95}$ = 13.8

Hatschek Homogenised Emulsion

16/11/26	Emulsion diln.	1:1300	x	-	-	-	25/2/27			
		1:1400	x	x	-	-		x	-	- -
		1:1500	x	x	-	-		x	x	- -
		1:1600	x	x	x	-		x	x	x -
		1:1700						x	x	x x
	Phenol diln.	1:95	x	x	-	-		x	x	- -

R.W. phenol coefficient = $\frac{1500}{95}$ = 15.8

Hunter Emulsion No. 3

		29/10/26	29/10/26	25/2/27
Emulsion diln.	1:1400	x - - -		
	1:1500	x x - -	x x - -	x x - -
	1:1600	x x x -	x x - -	x x x x
	1:1700	x x x x	x x x -	x x x x
Phenol diln.	1:95		x - - -	x x - -
	1:100	x x x -		x x x x
	1:105		x x x x	

R.W. phenol coefficient = $\frac{1600}{100}$ = 16 $\frac{1500}{95}$ = 15.8

These coefficients give the following values for unit amount of phenols present:-

Hatschek emulsion	13.8 ÷ 0.456 = 30.2
Hatschek homogenised emulsion	15.8 ÷ 0.487 = 32.4
Hunter emulsion	15.9 ÷ 0.499 = 31.9

The differences between the coefficient values per unit of H.B. tar acid are very slight and not so great as had been expected. The comparison with the emulsion particle size is given in the next section.

A comparison of the R.W. phenol coefficients of glue emulsions and castor-oil soap fluids (see p. 63) shows that, when the amount of H.B. tar acids present in both cases equals 50%, the value of the glue emulsion is 16 while that of the soap fluid is 21 (the average value of fluids B & C). The latter result indicates the important effect of the C.O. neutral oil upon the phenol coefficient value; confirmation of the effect is shown by the unit coefficient value of the H.B. tar acids increasing to 58.8 as the proportion of hydrocarbon oil in the soap fluids increases to

61% (Fluid A). The high R.W. phenol coefficients of the soap fluids cannot be attributed to the castor-oil soap, as in fluid D with C.O. neutral oil absent the comparison is in favour of the glue emulsions, when the coefficient value per unit of H.B. tar acid alone is considered.

DETERMINATION OF THE PARTICLE SIZE OF EMULSIONS AND COMPARISON WITH THE DISINFECTANT VALUE

T H E O R Y

Microscopical measurement is the method most generally adopted for the determination of the particle size of emulsions. The minimum size of the particles that may be viewed is dependent on the resolving power of the microscope, which is defined by the following equation:-

$$\text{Resolving Power} = \frac{\lambda}{2\mu \sin\alpha}$$

Where λ = Wave length of the illuminating beam of light.

μ = Refractive index of the medium between particle and lens.

α = Angle at which the lens is seen from the particle.

The limit of visibility with ordinary light is about 0.2μ. The Svedberg ("Colloid Chemistry" Chem. Catalog. Co., N.Y., p. 127) has calculated the limit of visibility of the commoner objective lenses, using the above expression, for light of $500\mu\mu$ wave length.

Dry lens	smallest	particle	visible	will be	$260\mu\mu$
Water immersion lens	"	"	"	"	200 "
Oil immersion lens	"	"	"	"	180 "
Ultraviolet light, $275\mu\mu$,	"	"	"	"	110 "

Zsigmondy and Spear ("The Chem. of Colloids" London, 1917, p. 19) say that the particle size near $200\mu\mu$ is of exceptional

interest in colloid chemistry, since at very slightly lower limits, 100$\mu\mu$ and under, particles of even high specific gravity remain suspended and in constant vibration, and at slightly higher limits Brownian movement is too small to be perceived. It is further stated that oil emulsions in water do not separate into two layers when the particle size is less than 0.8μ. This limit may be exceeded, however, and stable emulsions of larger particle size obtained when, according to Hatschek (Brit. Colloid Repts, 1918, 2, 17), the phase volume ratio approaches that of closest packing, e.g., in the creams which separate from many emulsions on settling, or when both phases have the same density. Such emulsions are not truly colloidal in character and their comparative stability will be less, owing to the greater probability of coalescence of the oil globules.

The stability of disinfectant emulsions is due to their small particle size, as the oil globules are seen to be in rapid Brownian movement when viewed under the microscope, or ultramicroscope. The practically negligible amount of settling prevents the determination of the distribution of the size of particles by settling experiments under the influence of gravity. This method has been applied with success to clays, and other fine suspensoids, by Oden (Proc. Roy. Soc. Edinburgh, 1916, 36, 219) Svedberg and Rinde (J.A.C.S., 1923, 45, 943) and W. J. Kelly ("Second Colloid Symp. Monograph", N.Y., 1925, p. 29). An

adaptation of the method to emulsion particles, which rise against the influence of gravity, has been advanced by Kraemer & Stamm (J.A.C.S., 1924, 46, 2709) and Stamm (2nd Coll. Symp. Mono. p. 70). Their results do not include data on emulsion particles less than 4μ to 6μ, which do not settle within 10 hours when Benzene is the disperse phase. Gravity settling, therefore, unless aided by centrifugal force (Svedberg and co-workers, J.A.C.S., 1923, 45, 2910; 1924, 46, 2677) or by an applied electric force (Burton and Reid, Phil. Mag., 1925), will be ineffective for the determination of the particle size of disinfectant emulsions.

Microscopical measurement by direct and indirect methods was attempted by the author, but only a small proportion of the total particles present could be observed and measured with accuracy. This result was unsatisfactory, as it seemed essential to measure the smaller rather than the larger particles in order to prove that the disinfectant value was increased by decrease in particle size. A method of determining the colloidal particles was necessary for this purpose.

Henri (Kolloid Z., 1913, 12, 246) reviews the different methods which have been employed for the determination of the size of colloidal particles, viz.:

(1) Direct count in the ultramicroscope.

(2) Method of determining density of the dispersion at different heights.

(3) Method of measuring Brownian movement.

(4) Estimation of particle size by measurement of velocity of settling.

(5) Estimation of particle size by diffusion.

(6) Estimation of particle size by light absorption.

(7) Estimation of particle size by light scattering effect.

The ultramicroscopic count is the simplest and most direct method, and it was decided to use this method as figures for the average particle size only were required. The slit ultramicroscope is the best type of instrument for particle size determinations, as the walls of the cell containing the colloidal solution under examination do not influence the counts and the colloidal solution in the cell is constantly being replaced by fresh material during the course of the examination. A slit ultramicroscope was not available, however, and the examination was conducted with a Cardioid Ultramicroscope, which gives better illumination than the earlier form of slit ultramicroscope but permits the examination of only a very small volume of the colloidal solution between chamber walls a few μ apart.

The diameters of colloidal particles cannot be directly measured in the ultramicroscope but merely the number of points of light from particles which make themselves visible by their scattering effect on the main beam of light, which does not enter the objective. The intensity of the

reflected light diminishes with the square of the volume of the particle (Siedentopf, Verhand. Deut. Phys. Gesell., 1910, 12, 1). Other factors influencing the intensity of the reflected light and, therefore, the degree of visibility of the particles are the refractive indices of the particle and the medium. Burton ("Physical Properties of Colloidal Solutions" London, 1921, p. 47) deduces from Lord Rayleigh's Law (ibid, p. 105) that the intensity of light diffused from a particle, small in all dimensions in comparison with a wave length of light, varies directly as the quantity:-

$$\left[\frac{\mu_1^2}{\mu^2} - 1\right]^2$$

where μ_1 and μ are the indices of refraction of the particle and the dispersion medium respectively. The refractive indices of oil emulsion particles compared with metallic colloidal particles are much nearer the refractive index of water and on this account the limit of visibility is reached at a greater particle size, but even with this limitation the method will demonstrate the existence of much smaller particles than is possible by microscopical means.

EXPERIMENTAL

Microscopical Examination of Soap-Fluid Disinfectant Emulsions

Direct measurement of Emulsion particles.

A 1:1000 dilution of Fluid B, containing approximately

40% of H.B. tar acids, was examined. The lenses in use were a No. 4 Leitz eyepiece and a 1/12th inch oil immersion objective. The apparent magnification of the combination was 1200, when obtained by projecting the image of a stage micrometer, by means of an Abbe Camera Lucida, on to a drawing board in level with the base of the microscope. The emulsion particles were seen to decrease in size from stationary spheres to very small spheres showing distinct Brownian movement. The larger particles did not exceed 2μ in diameter and the average size of 40 large particles which were traced on the drawing board and measured was 1.4μ. The smaller particles were present in greater number and the average diameter, which could not be measured with accuracy, was 0.4μ.

Indirect measurement of Emulsion Particles.

Direct measurement of particles approaching the limit of visibility of the microscope presents serious difficulty and the optional method of counting the number of particles within a definite volume of dilute emulsion was tried. A Zeiss haemacytometer slide was employed to define the volume of emulsion examined. The depth between the slide and cover slip was 1/10th mm, the areas enclosed by the transverse engraved lines 1/20th mm. apart were 1/400th sq. mm., and the volume of liquid above each area was 1/4000th cu.mm.

The prepared slide was placed flat on the stage of the

microscope, which was provided with a mechanical stage, and was viewed under the same lens combination as before. Three counts of Fluid B in 1:400, 1:1000, and 1:8000 dilution were made and the average diameter of the particles, by calculation, was 2.7μ, 3.1μ, and 2.5μ respectively. These high figures immediately indicated that all the particles were not being counted. The counting of the small motile particles was extremely difficult, as the depth of the emulsion was so great that all the particles were not in focus at the same time.

A possible large error was present in these preliminary experiments in the method of technique, due to the use of distilled water for the preparation of dilutions instead of water saturated with the oil phase of the emulsion. It was assumed also in the calculation that the soap went completely into solution but this could not cause serious error, as Riemann and van der Meulen (J.A.C.S., 1924, 46, 879) found that the soap adsorbed by the oil particles in 1:50 dilutions of phenol-toluene-sodium ricinoleate fluids was less than 1% of the oil phase.

Riemann and v.d. Meulen (ibid) adopted the following modified haemacytometer slide method for determining the size of the oil particles in their emulsions, as they were too small to count by the ordinary method.

> "The haemacytometer was first treated with a very dilute solution of stearin in ether containing not

> more than 0.8 mg per 10 cc, so as to form a very thin layer of the fat when the solvent evaporated. The globules on striking the glass were retained there by the fat. In about two minutes practically all the globules had affixed themselves to the slide. The globules in any square of the haemacytometer could easily be counted. To this count were added the globules remaining free in the liquid, and also the globules adhering to the cover glass immediately above that square. This number was equal to the number of globules originally contained in the volume whose dimensions are those of the square and the depth of the cell. A haemacytometer of 0.1 mm depth was used. For this determination the emulsion was diluted, one volume to 500, with water which had previously been shaken with an excess of oil of the same composition as the internal phase of the emulsion. Eight to ten squares were counted and the counts averaged."
>
> "A second method consisted in fixing the globules on the slide as described above and measuring them with a filar micrometer eyepiece. A 2 mm objective was used in both methods."

The emulsion particles were 1.242μ to 1.509μ diameter. The difference in results between the two methods was given as less than 0.2μ in every case and in most cases it was less than 0.1μ. The method promised well and was tried with soap fluid disinfectant emulsions.

The oil phase in Riemann and v.d. Meulen's concentrated fluids was a 20% by weight solution of phenol in toluene and Fluid A, containing 25% by volume H.B. tar acids in the oil phase, was employed in comparative experiments. A 1% emulsion was first prepared by the slow addition of 2 cc of the fluid to 198 cc of distilled water, which was being stirred mechanically by a propeller revolving

500 times per minute. The time of stirring was five minutes and 1:500 and 1:1000 dilutions were immediately afterwards prepared.

The haemacytometer slide and cover slip were cleaned and treated with a solution of 7.5 mgs cottonseed stearine in 100 cc anhydrous methylated ether. The ether was allowed to evaporate off under a bell jar and when dry the surfaces were covered with an even film of fat. A drop of 1:500 emulsion was placed on the slide and the cover slip carefully lowered on top. Examination after 1 hour showed that a few particles were held by the fat, 24 hours later a greater number were retained but the number still in motion was too great to be counted.

The method was further experimented with, using the quartz chamber and cover-slip of the Zeiss Cardioid ultramicroscopic outfit. The chamber resembles the haemacytometer slide but the depth of emulsion viewed is only a few μ compared with 100μ. The results of microscopical and ultramicroscopical examination after definite intervals of time are recorded in tables IX and X for the quartz slides treated with 7.5 mgs stearine in 100 cc petroleum ether; no better results were obtained when solutions of $2\frac{1}{2}$, 5 or $7\frac{1}{2}$ mgs stearine in 100 cc anhydrous methylated ether were employed.

TABLE IX

Combination of Lenses.

Zeiss focussing eyepiece K20x — Tube length 160 mm
Zeiss glycerine immersion objective 58V — Magnification 1160

Emulsion examined 1:500 dilution of fluid A in distilled water.
Depth of chamber 1:84μ

Time of observation after prepn. of slide	Number of particles observed, average of 10 counts: Microscopic examination: Vol. viewed	Fixed particles	Moving particles	Total No.	Calcd. diam.	Ultramicroscopic examinatn.: Vol. viewed	Fixed particles	Moving particles	Total No.	Calcd. Diam.
5 hours	524μ^3	4	5	9	0.56μ					
24 "	1069 "	14	6	20	0.55 "					
90 "	1069 "	21	3.5	24.5	0.51 "	524μ^3	24	22	46	0.33μ

TABLE X

Combination of lenses, as above
Emulsion examined 1:1000 dilution of fluid A in distilled water.
Depth of chamber 6.45μ

Time of observation after prepn. of slide	Number of particles observed, average of 10 counts: Microscopic examination: Vol. viewed	Fixed particles	Moving particles	Total No.	Calcd. diam.	Ultramicroscopic examinatn.: Vol. viewed	Fixed particles	Moving particles	Total No.	Calcd. Diam.
5 hours	1835μ^3	8	8	16	0.56μ					
24 "	3740 "	18	16	34	0.55 "					
90 "	3740 "	24	8	32	0.56 "	1835μ^3	31	40	71	0.34μ

Later experiments with a purer stearine, including the preparation of the emulsion without stirring and using distilled water saturated with the internal oil phase as

the diluent, did not make the oil globules adhere more readily to the fat. The substitution of palmitic acid in place of stearine gave no better result. The results, however, showed quite decisively, that the particle size closely approached the limit of visibility of the microscope and that ultramicroscopical methods must be employed in order to improve the accuracy of the determinations.

Ultramicroscopical Examination of Soap-Fluid Disinfectant Emulsions

The emulsions were first examined by the simple form of ultramicroscope devised by Cotton and Mouton (Compt. Rendu 1903, 136, 1657; "Les Ultramicroscopes", Paris, 1906). Burton (Phil. Mag., 1906, (6), 11, 425) used this apparatus in conjunction with a haemacytometer slide for determining the size of colloidal silver particles. The examination of the emulsions by this method proved that the emulsion particles were readily visible but satisfactory counts were not obtained for the following reasons:-

(1) The depth of the chamber was too great and all the particles could not be focussed at the same time.

(2) The engraved ruling of the haemacytometer slide reflected too much light and spoiled the effect of dark ground illumination.

(3) The slide and particularly the cover-slip, after scrupulous cleaning, never presented a perfectly black field during the examination of redistilled

> and settled water, free from ultramicroscopical particles. The surfaces were covered with round pin-points of light, like specks, which were believed to be due to imperfections in the surfaces of the glass. The specks could not be distinguished from small emulsion particles which had settled or been adsorbed by the glass, as, in contrast to colloidal metallic particles, the emulsion particles were colourless.

A Cardioid condenser and other fittings were obtained by my supervisor in order to obviate a number of the prominent defects in the above method of examination, and the following description summarises the method of setting up the apparatus.

The source of illumination was a small Westminster enclosed arc lamp, with the horizontal positive carbon pointing towards the microscope. The lamp was placed inside a photographic enlarger and the light rays, concentrated by the 6 inch lens of the enlarger, were projected on to the convex side of a concavo-convex lens, which transformed them into a parallel beam. The parallel beam of light passed through a heat absorbing solution of acidulated ferrous ammonium sulphate (20%), and was reflected into the Cardioid substage condenser by the mirror of the microscope. A drop of distilled water was placed on the top surface of the condenser and the chamber mount, with quartz chamber in position, was placed on the stage of the microscope. The Cardioid condenser was racked up until connected with the bottom of the quartz chamber by a stratum

of water, which was free from air bubbles. A drop of glycerine was placed on the cover-slip and the microscope lowered until the glycerine immersion objective made contact. The preparation in the cell was examined using a No. 4 (10x) Huygen's eyepiece, and adjustments made to bring the illuminated field into the vertical axis of the microscope. The condenser was now slightly racked up and down until the position of best illumination was attained and the Huygen's eyepiece replaced by the Zeiss K20x focussing eyepiece. Examination was conducted with this eyepiece and the Special Glycerine Immersion Objective V (58x), f = 3 mm, N.A. 0.85, which jointly gave a magnification of 1160 diameters.

Two points in the method of examination require detailing, viz., the method of determining the volume of liquid viewed and the type of quartz chamber with a description of the method of cleaning before use.

Determination of the Volume of Emulsion viewed.

In order to calculate this volume the surface area and depth must be known. Surfaces of definite area were therefore separated from their surroundings by the use of Ehrlich eyepiece stops with graduated square openings. The area of the field varied with different lens combinations and microscope tube lengths, and the area of each stop was therefore determined for the above lens combination and

definite tube length. A total tube length of 160 mm. was used. The area of the field separated was determined by comparing the dimensions of each stop against a stage micrometer. The image of the stage micrometer and of the stop, which was brought into focus by the eyepiece, were projected on to a ground glass screen and the lengths of the sides of the squares and of a 1/100 mm division of the stage micrometer were compared by measurement. The areas were found to be as follows:-

Stop No.	1,	Area	of	square	field	-	0.000285	sq.mm.
" "	2,	"	"	"	"		0.000580	"
" "	3,	"	"	"	"		0.001185	"
" "	4,	"	"	"	"		0.002400	"
" "	5,	"	"	"	"		0.004870	"
" "	6,	"	"	"	"		0.009750	"

The depth of the chamber was measured with the fine adjustment micrometer screw of the microscope, by focussing sharply in succession the top and bottom surfaces of the chamber and noting the displacement as recorded by the divisions on the periphera of the micrometer screw. The micrometer screw moved through four complete revolutions to the millimetre, and the micrometer head was marked off into 25 equal parts which were each further subdivided by slight notches on the periphera into 10 divisions. Each division on the periphera was therefore equal to 1/1000 mm = 1μ, and this degree of accuracy was obtainable in the measurement. It was customary to measure the depth of the

chamber between 10 and 20 times, over different parts of the field, but there was seldom much difference observed in the depths at different parts. The true thickness of the stratum of liquid in the chamber was found by multiplying the micrometer reading by the quotient of the refractive indices of the fluid in the chamber and the immersion fluid of the lens. The refractive indices of the emulsions, in the dilutions in which viewed, differed very slightly from distilled water; a maximum difference of 5 in the fourth place of decimals - and the above quotient was taken as a constant and equal to (1.3335 ÷ 1.4492) = 0.92, where 1.3331 was the refractive index of water and 1.4492 the refractive index of glycerine at 11.8°C.

Method of Cleaning the Cardioid Quartz Chamber.

The object slide, or bottom of chamber, resembles a haemacytometer slide without cemented joint. It consists of a circular disc about 20 mm. in diameter and 1 mm. thick, having on one side a circular groove, and within this groove an optically plane area which is about 2μ below the plane outside the groove. The optically plane cover is the same diameter and 0.75 mm. thick, which construction prevents it sinking upon the central portion of slide, lessens the danger of breakage, and facilitates cleaning. A fused quartz chamber has the following advantages over glass, viz., it does not fluoresce under intense illumination,

is less liable to corrosion and does not adsorb colloidal particles so readily. A special chamber mount is employed to facilitate the setting of the chamber in the correct position on the stage of the microscope.

The following instructions for cleaning the chamber are given in the Zeiss booklet, Mikro 306:-

"From the first the utmost care must be taken to prepare the surfaces in a faultless manner. This should be done in the first place by wet cleaning. To this end the slide should be cleaned thoroughly with alcohol and water, and rubbed with Japanese rice paper. Any small fibres which may adhere should be removed with a camel hair brush. The slide should then be suspended in a simple loop of stout platinum wire and dipped for a minute or two in an almost boiling mixture of concentrated sulphuric and chromic acids. Whilst being held in the platinum loop the slide should be thoroughly washed under the tap and then rinsed in distilled water. Next, about 15 cc. to 20 cc. of pure redistilled alcohol should be dropped upon its surface. The slide should then be allowed to drip and finally dried in a hot air current over a bunsen or by means of an electric heating arrangement. The slide should be placed by a clean pair of forceps in the chamber mount or upon some temporary support and allowed to cool under a glass bell. The cover requires a similar treatment and should be placed

upon the object-slide. After a little while broad Newton colour fringes of the first order will appear at the edges, if the surfaces have been properly cleaned."

Siedentopf (Verhandl.Deut. Phys. Ges., 1910, 12, 11) mentions that the distilled water and the new redistilled alcohol employed for cleaning must be macroscopically pure, and should not show any minute illuminated particles but merely a weak luminosity in the Tyndal cone, white with water and bluish with alcohol.

Distilled water, practically free from dust particles, was prepared by the careful redistillation of once distilled water followed by several weeks settling, as recommended by Zsigmondy ("Colloids and the Ultramicroscope" trans. Alexander, London, 1909, p. 112). Commercial 90/95% alcohol was purified by distillation with lime, then with metallic sodium and finally through a hard glass fractionating column packed with alcohol washed aluminium turnings. The distillate was condensed in a silica, or hard glass, condenser and received in a fused quartz flask. The condenser and flask were steamed out before use, and, on distillation, a little of the first part of the vapour was employed to further clean the condenser and flask, previous to putting water through the condenser jacket and collecting the distillate.

These precautions with the alcohol distillation were not immediately taken but were made in conjunction with

other attempts to improve the ultramicroscopical cleanliness of the quartz chamber. A perfect black field was never obtained, however, the disturbing element being a number of circular pin-points of light. Heating the slides to red heat, as recommended by Chamot ("Elementary Chemical Microscopy" London, 1915, p. 68), was no improvement. Biltz (Z. Chem. Ind. Kolloide, 1913, 12, 296) recommended the treatment of the slides with fused potassium bisulphate in a platinum crucible for the removal of adsorbed submicrons but even this did not achieve the desired freedom from specks. The slides were apparently perfectly clean and 2 mm Newton's rings were visible where the slide and cover were in contact.

The counting of the number of particles in emulsion dilutions was made extremely difficult owing to these specks and consistent counts of the adsorbed particles were not obtained. In control counts with ultrafiltered or distilled water, the average total number of specks on cover and slide per 0.000285 sq.mm. was usually between 1 and 2, the individual counts ranging between zero and five. The average number of adsorbed particles counted in soap fluid emulsion dilutions was seldom much greater than 2 and sometimes equal to the control number of specks previously determined. This result meant that no reliance could be placed on the counts of adsorbed emulsion particles,

as they could not be distinguished from the specks present during control counts. A number of examinations and counts proved, however, that the soap fluid emulsion particles were not adsorbed rapidly, as the increase in the fixed particles with time was never great and the decrease in the greater number of moving particles was slow; even in a chamber which had been treated previously with stearine the particles were in motion after 90 hours. These results led finally to the adoption of the counting of the moving particles alone as a measure of the particle size and dispersion of the emulsions.

Preparation of Dilutions of the Disinfectant Fluids.

In order to prevent solution of either phenols or oil on dilution of the fluid, it was necessary to saturate the water employed for dilutions with the internal oil phase of the fluid and to remove suspended oil particles by ultrafiltration. Hatschek ("Laboratory Manual of Colloid Chemistry" p. 72) details Oswald's methods of preparing spontaneous and vacuum ultrafilters. The best results were obtained by spontaneous ultrafiltration and the ultrafilters were prepared finally, as follows:-

A 25 cm. circle of No. 1 Whatman paper was folded twice in the usual way and carefully fitted into a well-shaped smooth glass funnel. The filter was filled to the edge with 2% Acetic Acid collodion and the excess was later

poured off, after the collodion had penetrated the paper over the entire surface. The filter was immersed overnight in running water and distilled water was passed through the filter on the following day, previous to introducing the oil-saturated water which required ultra-filtration. The rate of filtration was about 750 cc. in 24 hours and the first 100 cc of the filtrate was discarded, since it sometimes contained a number of ultramicroscopical particles. Filtration was conducted in the dark, as it was observed that ultrafiltered water, saturated with H.B. tar acids or a mixture of H.B. tar acids and C.O. neutral oil, became pink and opalescent on exposure to light for 12 hours or more. This change was probably due to air oxidation accelerated by light, as it was retarded but not prevented by storage in the dark. The number of ultramicroscopical moving particles in freshly filtered oil-saturated water was small and did not exceed 1 in 5000μ^3. In water, a week old, which was pink and slightly opalescent, the number of moving particles had increased to about 4 in 5000μ^3. Freshly ultrafiltered water was employed in all the ultramicroscopical counts and the number of particles determined before proceeding with emulsion counts.

Emulsions were prepared from the soap fluid disinfectants by 15 minutes' mechanical shaking of a 2½% dilution of the fluid in ultrafiltered water saturated with the oil phase, as fully described on page 59. This emulsion was

immediately diluted, in several steps, to a 1:40,000 or 1:80,000 concentration of the fluid. The bottles or measuring cylinders were rinsed with ultrafiltered water before use. No ground glass stoppers were used and containers were stoppered with corks coated with tin foil. The very high dilution of the fluid was required in order to reduce the number of moving particles in the volume examined to about four, which number could be counted at a glance. A mechanical stage on the microscope assisted in systematically covering the field and about 100 observations were made at $\frac{1}{2}$ mm. intervals over the chamber area. A statistically sufficient number of counts was required in order to obtain a proper average, but many other factors affect the accuracy of ultramicroscopical results and Kuhn (Kolloid Z., 1925, 37, 365) estimates the error, with satisfactory illumination, at 10% to 20%.

Photochemical Effect of Intense Illumination on the Emulsions.

The results of early counts were inconsistent, as the numbers of particles in equal volumes of the emulsions varied from 1 to 12. The cause of this wide variation was ultimately traced to the photochemical action of the intense illumination obtained at the focal point of the Cardioid Condenser. The action of the light was to increase the number of particles observed. After 1 to 2 minutes' exposure a number of very small rapidly moving particles

began to appear and these increased in size and brightness until, within less than 5 minutes in many cases, the number of plainly visible moving particles was infinitely great and could not be counted in a volume of $500\mu^3$. The particles which formed were not rapidly adsorbed by the walls of the chamber and, after 45 minutes' exposure, many more particles were in motion than were adsorbed. The photochemical effect was only apparent when the image of the crater of the arc lamp was accurately focussed within the chamber and the depth of the chamber did not exceed about 4μ. A similar photochemical effect was observed with the ultrafiltered water which had been saturated with H.B. tar acids or mixtures of these acids with C.O. neutral oil. No photochemical effect was observed in solutions of pure phenol or p/cresol, or in the case of water which had been saturated with excess p/cresol and ultrafiltered.

Siedentopf (Verhandl. Deut. Phys. Ges., 1910, 12, 34) recommends the use of the Cardioid ultramicroscope for the study of photochemical changes and reports the action of this intense illumination on colloidal gold, silver and platinum solutions, on dyestuffs and on silver halogen salt solutions. The light reactions proceed from reduction or oxidation, and permit the supposition of the decomposition of the water, etc., in the vicinity of the light. The bleaching of colloidal gold, silver, or platinum particles

is explained by oxidation and reduction is indicated for the separation of particles from a crystalloidal solution of potassium bichromate. The light transformations proceed quantitatively by themselves; the change in a defined point appearing not to influence temporarily the change in neighbouring points which lie only 0.3μ distant. The photochemical actions are said to proceed normally when blue glass is interposed in the illuminating beam but are completely retarded by the interposition of red glass. Biltz (Z. Chem. Ind. Kolloide, 1913, 12, 296) has studied similar photochemical reactions in the Cardioid ultramicroscope and has observed the production of submicrons from Fehling's solution, 5% sodium nitroprusside, and 1% sulphur in carbon disulphide. Weigert (Sammlung Chem. u. Chem. Tech. Vortrage, 1912, 17, 183/296) very completely reviews the chemical action of light, and oxidation is there regarded as one of the catalytic effects of light reactions.

High boiling tar acid solutions contain fairly soluble products which are readily oxidised, particularly in presence of sodium hydroxide, and are the cause of the pink colour of emulsions or of aqueous solutions from low temperature tars. Burke and Caplan (J.I.E.C., 1924, 19, 34) have found these products to be ortho dihydroxy derivatives of aromatic hydrocarbons, e.g., 3:4 or 3:6 dimethyl

pyrocatechol, which are slightly soluble in cold water, are readily oxidisable with ferric chloride, and with air in presence of sodium hydroxide yield a final non-reducible substance, in relation to which the red colour body is an intermediate product. It may be, therefore, that catalytic oxidation by the action of light at the focus of the Cardioid ultramicroscope converts these soluble products in the ultrafiltered aqueous extracts of H.B. tar acids into insoluble substances, which appear spontaneously in the field of view as submicrons and gradually increase in size as the action progresses.

The photochemical action of the light on emulsions, or on ultrafiltered water saturated with the emulsion oil phase, was prevented by placing a red glass screen in the path of the illuminating beam. The setting in position and focussing of the chamber was done, therefore, under red light. The red screen, however, greatly decreased the visibility of the particles and during counts it was found necessary to remove the screen for the few seconds taken up by each count in different positions in the field. The particles did not increase during this short interval and neighbouring areas of the slide were unaffected. With this technique fairly consistent counts and average particle size determinations were made possible. The following example illustrates the method, and details the calculation of the average diameter of the oil globules.

Calculation of the Average Diameter of Emulsion Particles
Sodium Castor-Oil Soap Fluid A

Oil phase in fluid:- 20.4% by volume H.B. tar acids and
61.2% by volume C.O. neutral oil, a
total of 81.6% disperse phase.

Examination of Ultrafiltered Water saturated with the Oil Phase.

No. of counts		88
Total No. of motile particles observed		17
Area of field examined during each count		1,185μ^2
Depth of chamber measured by micrometer of microscope		5μ
Actual depth of chamber	$= \frac{5\mu \times \text{Ref.Ind.water}}{\text{Ref.Ind.Glycerine}}$	
	$= 5 \times 0.92$	$= 4.6\mu$
Volume examined	$= 1{,}185\mu^2 \times 4.6\mu$	$= 5{,}540\mu^3$
Average No. of motile particles per $5{,}540\mu^3$	$= 17 \div 88$	$= 0.19$

Examination of 1:40,000 dilution of Fluid A.

No. of counts	79
Total No. of motile particles observed	284
Average No. of " " per count	3.6

Analysis of counts

In	2	counts	1	particle	was	observed	= total 2
"	14	"	2	particles	were	"	" 28
"	23	"	3	"	"	"	" 69
"	21	"	4	"	"	"	" 84
"	14	"	5	"	"	"	" 70
"	4	"	6	"	"	"	" 24
"	1	"	7	"	"	"	" 7
							Total 284

Area of field examined during each count			285μ^2
Depth of chamber, microscope micrometer reading			3μ
Actual depth of chamber	$= 3\mu \times 0.92$	=	2.76μ
Volume examined	$= 2.76\mu \times 285\mu^2$	=	$785\mu^3$

In 785×10^{-9} cu.mm. of emulsion there were 3.6 particles
" " " " ultrafiltered water 0.03 "
No. of particles from emulsion alone = 3.57

3.57 particles in 785×10^{-9} cu.mm. of 1:40,000 dilution
3.57 " " $\frac{785 \times 10^{-9}}{40,000}$ " " Fluid A

3.57 " " $\frac{785 \times 10^{-9} \times .816}{40,000}$ cu.mm. oil phase

1 " " $\frac{785 \times 10^{-9} \times 0.816}{40,000 \times 3.57}$ " " "

$$\text{Radius of 1 particle} = \sqrt[3]{\frac{3 \times \text{Vol. of 1 particle}}{4 \times \pi}}$$

$$= \sqrt[3]{\frac{3 \times 785 \times 10^{-9} \times 0.816}{4 \times 40,000 \times 3.57 \times 3.142}}$$

$$= 102 \times 10^{-6} \text{ mm.}$$

Average radius of one emulsion particle = 102 $\mu\mu$
" diameter " " " = 204 $\mu\mu$

The results of four counts for the sodium castor-oil soap fluids A, B, C and D are given, with full details of the determinations, in table XI. The maximum difference between any two estimations of the particle size for the same fluid does not exceed 6%. A greater degree of accuracy was hoped for but was not obtained, owing to the extent of variation between individual counts and a possible error of 0.5μ in the measurement of the chamber depth.

TABLE XI

Ultramicroscopical determination of the particle size of sodium castor-oil soap disinfectant emulsions.

Fluid	Dilution	Depth of Chamber. Direct reading μ	Volume examined μ^3	Av.No of part. in water	Av.No of part. emulsion	No.of Counts	Minm. No part. obsvd	Maxm. No part. obsvd	Calcd. diam. emulsion part. $\mu\mu$	Av. dia. $\mu\mu$
A	1:40,000	3	785	0.03	3.60	79	1	7	204	
"	1:40,000	2	525	0.10	2.74	86	-	6	198	203
"	1:40,000	5	1310	0.16	6.33	80	3	10	202	
"	1:80,000	5	1310	0.05	2.91	86	1	7	208	
B	1:40,000	2	525	0.10	2.90	93	-	6	196	
"	1:40,000	2	525	0.04	2.5	85	-	6	204	
"	1:80,000	2	525	0.08	1.3	78	-	3	204,	201
"	1:80,000	5	1310	0.05	3.30	80	1	6	200	
C	1:40,000	2.5	655	0.04	2.04	75	-	4	231	
"	1:40,000	2	525	0.06	1.87	81	-	4	222	226
"	1:80,000	3	785	0.04	1.45	80	-	4	218	
"	1:80,000	5	1310	0.12	2.13	73	-	4	230	
D	1:20,000	1.75	459	0.03	1.11	90	-	3	310	
"	1:40,000	4	1050	0.06	1.41	78	-	4	300	
"	1:40,000	5	2670	0.14	3.09	94	1	5	316	309
"	1:80,000	6.5	1705	0.09	1.1	103	-	3	310	

Comparison of the Emulsion Particle Size and Disinfectant Value of Soap Fluids.

The accuracy of the method has been insufficient to show that the average particle size of fluid A is definitely greater or less than fluid B, but the results show a decided increase in the average particle size of fluids C and D. The average diameters of the particles are compared with

the disinfectant values of the fluids in Table XII, and it is there observed that, in fluids C and D, where the decrease in the coefficient value per unit of phenol is greatest there is an accompanying increase in the average particle size of the emulsions. This result supports the view that a decrease in particle size increases the germicidal activity of the emulsions. The very large increase in the average particle size of Fluid D and the decided drop in the phenol coefficient value of this fluid, compared with the other three fluids which contain neutral hydrocarbon oil, confirms the statement of Kenwood (M.O., 1926, 35, 121) that the addition of neutral oil to high boiling tar acids increases the germicidal action because a finer emulsion is formed.

TABLE XII

Fluid	H.B.tar acids %Vol.	C.O.N. oil %Vol.	Anhyd. soap %Vol.	Water %Vol.	R.W. coeff.	Coeff. /unit oil phase	Coeff. /unit H.B. acids	Av.Diam. emulsion particles μμ
A	20.4	61.2	8.8	9.6	12	14.7	58.3	203
B	41.9	41.9	9.9	6.3	20	23.9	47.7	201
C	58.9	19.7	12.7	8.7	22	28.0	37.3	226
D	73.3	-	18.0	10.8	18	24.6	24.6	309

The effect of a difference in the refractive indices of the oil phase on the visibility has not received consideration in the above comparison. The refractive indices of the oil phase in the above four fluids and the relative

intensity of the light diffused from the particles, as determined by the expression $I \propto \left[\frac{u_1^2}{u^2} - 1\right]^2$, are given in Table XIII. The final column in the table was obtained by dividing the average number of particles visible in each count by the intensity factor in column 5 and recalculating the average diameter.

TABLE XIII

Fluid	Ref.ind.of dispersed oil phase u_1	Ref.ind.of dispersion medium u	$I \propto \left[\frac{u_1^2}{u^2} - 1\right]^2$	Intensity relative to A.	Recalculated av. diam. of particles $\mu\mu$
A	1.5728	1.3335	0.1522	100	203
B	1.5644	"	0.1406	92.4	196
C	1.5561	"	0.1303	85.6	214
D	1.5481	"	0.1212	79.6	286

It is seen, therefore, that even with this allowance for the difference in intensity of the light diffused by the emulsion particles, the average diameters of the oil globules in fluids C and D are greater than in the other two fluids. The apparent increase in the diameter of the emulsion particles from fluid A compared with fluid B may be due to the nature of the interfacial film surrounding the emulsion particles. In the fluids with higher proportions of phenols than A, the phenols may have replaced part of the soap in the interfacial film and thus increased the visibility of the oil particles compared with A. This reasoning is

suggested by the results of Riemann and v.d. Meulen (J.A.C.S., 1925, 47, 2507) which proved that phenol could form part of the interfacial film, and by the results of the examination of glue emulsions which are given later.

The germicidal power of sodium oleate fluids has been found considerably less than sodium castor-oil soap fluids and the following result indicates that this decrease in efficiency may be accounted for, at least in part, by the difference in the average size of the emulsion particles.

TABLE XIV.

Fluid	H.B.tar acids %Vol.	C.O.N. oil %Vol.	Anhyd. soap %Vol.	Water %Vol.	R.W. phenol coeff.	Coeff. /unit oil phase	Coeff. /unit H.B. acids	Av.Diam. emulsion particles μμ
Castor-oil soap fluid B	41.9	41.9	8.8	9.6	20	23.9	27.7	201
Sodium oleate fluid	38.5	38.5	11.0	12.0	10.5	13.7	27.3	250

No results on the emulsion particle size of blast furnace neutral oil fluids have been obtained, as time was too limited towards the end of the period of research to undertake a study of the effect of the nature of the hydrocarbon oil on the disinfectant value and emulsion particle size of

soap fluids. The ease of emulsification and the slow settling of emulsions of these fluids in water are opposed to the view that the decrease in germicidal activity is caused by a wide difference in the size of the emulsion particles and, indeed, suggest that the nature of the hydrocarbon oil is alone responsible.

Ultramicroscopical Examination of Glue Emulsion Disinfectants

The glue emulsions which were prepared by the Hatschek and Hunter emulsifiers were examined. The preparation of the dilutions differed from the soap-fluid emulsions, as mentioned previously p. 60, only by the elimination of the mechanical shaking of the preliminary 2½% emulsion.

Fewer particles were visible in the glue emulsions than in similar dilutions of the soap fluids. The photochemical effect of intense illumination at the focus of the Cardioid condenser was generally apparent within a shorter period, ½ minute to 1 minute, and the particles which formed were more readily adsorbed on the walls of the chamber. The method was found inapplicable to emulsions prepared by the "Hunter" Emulsor, as too few motile particles were visible in the field even in a 1:8000 dilution. When, however, the initial 2½% emulsion had been mechanically shaken for 15 minutes and then diluted, more particles became visible and the average diameter, calculated from the motile particles alone, was found to be about 400 uu. This difference in

visibility of the particles may be accounted for by the unshaken dilutions containing particles below visible size or, alternatively, the shaking may have partly removed the protective film of glue which makes observation more difficult. The emulsion particles in the Hatschek and homogenised emulsions were visible under the ultramicroscope, and it would appear that the protective glue film was partially stripped from the oil globules during emulsification by these methods. The results of the ultramicroscopical examination of the Hatschek emulsion and of this emulsion after homogenisation, as described on page 70, are given in Table XV.

TABLE XV.

Emulsion	Dilution	Depth of chamber. direct reading μ	Volume examined. μ^3	Av.No. of part. in water	Av.No. of part. emulsion	No.of counts	Minm. No. part. obsvd	Maxm. No. part. obsvd	Calcd diam. emulsion part. $\mu\mu$
Hatschek	1:8,000	5	1310	0.07	3.60	104	1	6	342
"	1:8,000	5	1310	0.07	3.42	72	1	5	348
Homogenised	1:8,000	4	1050	0.05	3.57	86	1	7	326
"	1:20,000	5	1310	0.04	1.95	80	-	4	318

TABLE XVI

Emulsion	H.B.tar acids % by vol.	R.W.phenol Coeff.	Coeff.per unit H.B. tar acid	Average emulsion particle size
Hatschek	45.6	13.8	30.2	345 $\mu\mu$
Homogenised	48.7	15.8	32.6	322 "

The increase in germicidal value coinciding with decrease in particle size is again shown by these results, although the differences are not great. The addition of hydrocarbon oil to the glue emulsions also caused a decrease in the particle size, a result which confirms the previous results with soap fluids. The observed decrease in the emulsion particle size of Hatschek prepared emulsions was from 345$\mu\mu$ to 326$\mu\mu$, when the C.O. neutral oil represented 20% of the oil phase. The value 326$\mu\mu$ compares with that of the homogenised emulsion, and settling tests in 10% dilution of the two emulsions were also comparable.

Comparisons between the ultramicroscopical results obtained with glue and castor-oil soap fluid emulsions show that the particle size of the glue emulsions is considerably larger than the particle size of the soap fluid emulsions when the volume of H.B. tar acids present in each case is the same and the soap fluid emulsion contains, in addition, hydrocarbon oil. Comparisons of the germicidal activity of the phenols in the same two types of emulsions, as determined by the unit coefficients of the H.B. tar acids present, show that the phenol coefficient value of the glue emulsions is less than that of the soap fluid emulsions containing hydrocarbon oil. The relationship between small particle size and high phenol coefficient value is therefore apparent when soap fluid emulsions having hydrocarbon oil present are considered. The same relationship is not found, however,

when a comparison is made between the particle size and corresponding phenol coefficient value of glue and castor-oil soap fluid emulsions containing no hydrocarbons. In this case the relative germicidal value, as determined by the unit phenol coefficient value of the H.B. tar acids present, is shown to be higher with the glue emulsions although the particle size of the soap fluid emulsion is slightly less. The ultramicroscopical particle size determinations of soap and glue emulsions may not be strictly comparable, however, on account of the much greater difficulty found in viewing the particles of the glue emulsions, a difficulty which also applied partly in the case of the soap fluid emulsion with hydrocarbon oil absent.

Microscopical Examination of Glue Emulsion Disinfectants.

Microscopical examination of the glue emulsions was substituted for the ultramicroscopical, in order to obtain comparative values of the particle size of the Hatschek and Hunter emulsions. The best conditions for viewing the emulsions were obtained with a 1/12th inch oil immersion objective and No. 4 (10x) eyepiece combination, when the depth of the chamber containing the emulsion was not too great. The Cardioid quartz chamber with a glass cover slip in place of the quartz cover was fitted in the chamber mount, and viewed by direct illumination with the above lens combination. Fairly consistent counts of the oil globules within a definite volume were obtained, but the calculated

diameter was very much greater than that derived from ultra-microscopical examination. The results are recorded below in tabular form and the calculated emulsion particle size is compared with the disinfectant value.

TABLE XVII

Emulsion	Diln.	Depth of chamber, direct reading μ	Vol. examined μ³	Particles fixed on slide per count			Motile particles per count			No. of Counts	Calc. diam. total particles μ	Calc. diam. motile part. only μ
				Min. No.	Max. No.	Aver. No.	Min. No.	Max. No.	Av. No.			
Hatschek	1:200	3	1290	-	7	3.0	1	6	2.95	78	0.98	1.24
"	1:200	4.5	1935	-	7	4.06	1	7	4.39	72	1.00	1.24
Briggs	1:200	3	1290	1	10	3.70	1	7	4.0	68	0.92	1.14
Homogenised	1:200	3.5	1505	-	7	4.0	1	6	4.5	70	0.93	1.13
Hunter	1:200	4.5	1935	-	7	1.64	4	10	6.13	94	1.06	1.14
	1:200	10	2210	-	10	4.0	2	9	6.7	72	0.99	1.15

The high result for the average diameter calculated from the total particles in the count of the Hunter emulsion was due to greater difficulty in viewing the very small unstained oil globules, and it would appear that a number of the smallest particles have been missed in these two counts. The counts of the motile particles were more consistent and the average particle size was calculated from the motile particles only, as a measure of the degree of dispersion. The comparison of these results with the disinfectant value of the emulsions, shown in table XVIII, follows the course

of previous determinations and supports the contention that the germicidal activity of the phenols is increased by increasing the fineness of the emulsions.

TABLE XVIII

Emulsion	Density 15.5°C	H.B.acids % by wt.	H.B.acids % by vol.	R.W. Coeff.	Coeff.per unit vol. H.B.acid	Emulsion particle size
Hatschek	1.0228	45.8	45.6	13.8	30.2	1.24μ
Briggs homogenised	1.0235	48.9	48.7	15.8	32.6	1.135μ
Hunter	1.024	50.2	49.9	15.9	32.0	1.145μ

Increase in Disinfectant Value of Glue Emulsions compared with the Increase in Dispersion produced by Homogenisation.

The dispersion of the emulsions is inversely proportional to the average size of the emulsion particles, and in Table XIX the increase in the disinfectant value of the Hatschek emulsion by homogenisation is compared with the increase in dispersion, as determined from ultramicroscopical and microscopical counts.

TABLE XIX

	Hatschek Emulsion (a)	Homogenised Hatschek emulsion (b)	Effect of homogenisation: Increase in disinfectant value $\frac{(b-a)100}{a}$	Effect of homogenisation: Increase in dispersion $\frac{(a-b)100}{b}$
R.W. phenol coeff per unit H.B. acid	30.2	32.6	7.9%	
Emulsion particle size				
Ultramicroscopical count	0.345μ	0.322μ		7.1%
Microscopical - total particles	0.99μ	0.925μ		7.0%
Microscopical - motile particles	1.24μ	1.35μ		9.2%

These results are therefore in agreement with the statement of E. K. Rideal (5th Rept. on Colloid Chem., p. 37, 1923) that "In the preparation of the emulsified disinfectants "the germicidal power for a given tar acid content is nearly proportional to the fineness of the emulsion."

GENERAL CONCLUSION

The study of the preparation of disinfectant emulsions containing phenols and the comparison of their germicidal value with the degree of dispersion have shown that the stability and germicidal values increase with the fineness

of the emulsions. The finest emulsions were formed by castor-oil soap fluid disinfectants and the maximum dispersion was obtained when the volume of phenols in the fluid did not exceed the volume of coke-oven neutral oil present. Such fluids were more highly dispersed than glue emulsions or soap fluids, containing no hydrocarbon oil, and the germicidal value was also greater although a lower percentage of phenols was present.

PART III

EFFECT OF SLIGHT VARIATION IN THE ADJUSTMENT OF THE ACIDITY OF RIDEAL-WALKER BROTH UPON THE PHENOL COEFFICIENT VALUE OF COAL-TAR DISINFECTANTS

INTRODUCTION

A very disturbing factor met with at the commencement of the testing of disinfectant fluids was that the phenol coefficients, determined for a number of commercial preparations of guaranteed Rideal-Walker value, were approximately 70% of the values claimed. Consistent values at this ratio were obtained and a reason for the low results was naturally sought.

Many investigators have reported their inability to obtain the high coefficient values which are guaranteed by manufacturers of disinfectants, or reported by the authors of the test. Fairbrother & Renshaw (Indus. Chem., 1925, 1 371), to cite one example, state that they have never obtained a higher value than 12, even for a fluid with alleged coefficient over 20. A paper (J. State Med., 1923, 31, 477) from the laboratories of the Royal Institute of Public Health records wide variations in the coefficients of the same disinfectants, as obtained by a number of well-known bacteriologists. In this paper, as well as in a previous paper from the same laboratories (ibid, 1919, 27, 53), most of the factors responsible for variation are discussed, but no experimental data is given on the standardisation of the broth.

S. & E. K. Rideal ("Chemical Disinfection and Sterilisation" London, 1921, p. 294) say, regarding the method of

standardising the broth, that "Neither the original Rideal-Walker nor the Hygienic Laboratory broth is sufficiently uniform when made up by different investigators to give reproducible results, even with a limitation of the phenol control periods for the organism as stipulated in the present-day test". J. H. Wright (J. Bact., 1917, 2, 315/346) reviews in detail the problem of uniformity in culture media, and shows that the phenol coefficient of a disinfectant varies with the hydrogen-ion concentration of the media.

The present author found that the coefficient value of disinfectants varied slightly on different batches of media in which the acidity, as ascertained by pH determinations, was not identical and further work, with a view to account for these results, pointed to the standardisation of the broth being mainly responsible. The revised instructions for the preparation and standardisation of the broth, which S. Rideal and J. T. A. Walker give in a brochure on the "Approved Technique of the Rideal-Walker Test", published by H. K. Lewis & Co., Ltd., London, 1921, do not state whether the broth is neutralised to phenolphthalein in the cold, according to customary chemical practice when using this indicator, or at the boiling point of the broth, according to bacteriological practice as recommended by Eyre ("Bacteriological Technique" 2nd Edn., London, 1916,

p. 149). This difference in the method of neutralisation was found to alter the final reaction of the broth and caused differences in the phenol coefficient values of the disinfectants.

The investigations of Eyre, which led to his recommending the boiling point titration, were published previous to the original presentation of the Rideal-Walker technique for testing disinfectants (J. Roy. San. Inst., 1903, 24) and it was possible, therefore, that this method of titration was employed. Subsequent investigations do not support Eyre's recommendation, as the statement that "the hydrolysis of nutrient broth ceases after 45 minutes boiling" has not been confirmed by the experiments of Anthony & Ekroth (Collected Studies N.Y. Bur. of Lab., 1914/15, 8, 294), and Clark (J. Inf. Dis., 1915, 17, I, 109) classifies as erroneous a further statement that "the correct estimation of acidity can only be made at the boil". Clark determined that the difference in the final acidity of the broth, when titrated in the cold or at the boiling point, was equivalent to between 0.5% and 1% of N/1-HCl. This difference between the methods of titration is of extreme importance since Rideal-Walker broth has to be adjusted to 1½% acidity, without knowledge however of the method of titration.

The investigations conducted by Clark & Lubs (J. Bact. 1917, 2, 1, 109, 191) have proved that titration methods are

unreliable for the standardisation of biological media and that it is essential to control the acidity of media on the basis of the hydrogen-ion concentration. Many standard media, therefore, are now adjusted to a definite pH value instead of by titration, and the reaction to which most bacteriological media are brought is pH 7.6. This reaction corresponds with that of plasma. No official statement of the reaction of Rideal-Walker broth has been found in the literature but pH 7.65 is given by Wright (J. Bact., 1917, 2, 315).

EXPERIMENTAL

The method of carrying through the tests and of determining the phenol coefficients was in accordance with the revised instructions given by the authors, S. Rideal and J. T. A. Walker, in the brochure already mentioned, except for the modifications given below.

Culture

The test organism, a pure culture of the "Lister" strain of Bacillus Typhosus from the National Collection of Type Cultures, was maintained at room temperature on Agar, pH 7.5, and transferred at monthly intervals to fresh agar slopes. The broth test cultures were inoculated from a

month old agar slope of the test organism and subcultured daily at the same hour for five days previous to the test, in order to obtain comparative results. The fifth day's subculture was chosen for two reasons: first, it had been found that the resistance of the test organism to phenol progressively decreased up to the third day's subculture before becoming constant, and secondly, as reported from the Royal Instit. of Public Health (J. State. Med., 1919, 27, 53) and observed by the author on one occasion, because the phenol coefficient of an emulsion disinfectant decreased in value with the age of the culture, as determined by the number of subcultures. These results were as follows:-

TABLE XX

Decrease in resistance of B. Typhosus to phenol by subculturing.

Phenol dilution	Number of days subcultured in broth															
	One				Two				Three				Four				Seventeen			
	Time Culture in contact with disinfectant - Minutes															
	2½	5	7½	10	2½	5	7½	10	2½	5	7½	10	2½	5	7½	10	2½	5	7½	10
1:90	x	x	-	-	x	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1:100	x	x	x	x	x	x	x	-	x	-	-	-	-	-	-	-	-	-	-	-
1:110	x	x	x	x	x	x	x	x	x	x	-	-	x	x	-	-	x	x	-	-

The number of consecutive day's subculturing is not specified in the Rideal-Walker test but Reddish (J. Amer. Pub. H., 1927, 17, 321) recommends 3 days, the American Hygienic Lab. Method insists on at least 5 days, and Wright used only the 7th day's subculture.

TABLE XXI

Decrease in phenol coefficient of emulsion disinfectant by subculturing.

Disinfectant	Dilution	Number of days B.Typh. subcultured in broth											
		Five				Nine				Seventeen			
		Time Culture in contact with Disinf. - Mins.											
		2½	5	7½	10	2½	5	7½	10	2½	5	7½	10
Fluid B	1:2200	x	-	-	-	x	-	-	-	x	x	-	-
	1:2400	x	-	-	-	x	-	-	-	x	x	x	x
	1:2600	x	x	x	-	x	x	-	-	x	x	x	x
	1:2800	x	x	x	x	x	x	x	x	x	x	x	x
Phenol	1:110	x	x	x	-	x	x	-	-	x	x	-	-
R.W. Phenol Coeff.		about 23.6				23.6				20			

CULTURE MEDIUM

The broth was standardised by titration, using phenolphthalein as indicator, and the reaction of the broth was checked by colorimetric pH determinations. The pH values were determined by L. J. Gillespie's indicator method (J.A.C.S., 1920, 42, 744) and by W. D. Hatfield's modification of the same method (ibid, 1923, 45, 940). The pH values recorded by Gillespie's method were found to agree with values obtained by Clark & Lubs colorimetric method (J. Bact., 1917, 2, 1, 109, 191) using standardised buffer solutions, and to correspond with hydrogen electrode determinations as follows:-

TABLE XXII

Comparison of pH determinations

Electrometric pH	Clark & Lub's method		Gillespie's method	
	Brom. Thymol Blue	Phenol Red	Brom. Thymol Blue	Phenol Red
6.58	6.6	-	6.7	-
6.97	7.0	-	6.9 - 7.1	-
7.23	7.2	7.2	7.1 - 7.3	7.2
7.40		7.4		7.4
7.65		7.7		7.7

Three separate broths were prepared in the following manner, in order to determine the effect of unintentional variation of acidity resulting from different methods of titration.

Broth (a):- The ingredients, 20 g. of "Lemco", 20 g. of Allen & Hanbury's "Eupepton", and 10 g. of pure sodium chloride, were dissolved in 1 litre of distilled water by boiling for 30 minutes, and the resulting broth was filtered, then cooled. 10 c.c. of the broth were diluted with 50 c.c. of boiled and cooled distilled water and titrated with 0.1N - sodium hydroxide in the cold, after the addition of 10 drops of a 0.5% alcoholic solution of phenol-phthalein. A control vessel with the original diluted broth was kept alongside during the titration, since the end-point chosen was the first faint but distinct pink tinge. The calculated quantity of N-sodium hydroxide required to neutralise the remainder of the broth was added, the neutralisation checked

by phenolphthalein, and the pH value determined. The pH value of the broth at this stage was found to be 8.2. 15 c.c. of N-hydrochloric acid were now added, and the broth was boiled 30 minutes, filtered, made up to 1 litre, and sterilised. The broth was boiled after acidification in order to prevent precipitation during sterilisation, which always occurred if this precaution was omitted. The pH value of the broth after filtration was 6.9.

Broth (b):- The broth, containing the same ingredients as above and in identical proportions, after preliminary solution and filtration was made neutral to phenolphthalein at the boiling point of the broth by the addition of the calculated quantity of N-sodium hydroxide, determined from the titration of an aliquot portion at the boil. The broth was boiled 15 minutes at this stage and the neutralisation checked against phenolphthalein. By this method of neutralisation the pH value of the neutral broth was found to be 8.6. 15 c.c. of N-hydrochloric acid were added, the broth was boiled 30 minutes, filtered, made up to 1 litre, and sterilised. The pH value of the broth after filtration was 7.3.

Broth (c):- To assist in correlating results, broth prepared as in (b) was adjusted to pH 7.6 by the addition of N-sodium hydroxide. Precipitation was found to occur during sterilisation, and the broth was heated to boiling and refiltered.

Sterilisation increases the acidity of nutrient broth

but this factor does not affect the present comparison, since all broths were sterilised in a similar manner. The acidity of Rideal-Walker broth increases by about 0.1 pH on sterilisation, and by 2 to 3 times this figure when kept for a few months in flasks stoppered with cotton wool, which does not prevent the entrance of carbon dioxide.

Disinfectant Fluids

Fluids A and B, referred to in table XXIII, are the sodium castor-oil soap fluids described previously page 36, they are comparable with medium- and high-coefficient commercial preparations. "Medical Cyllin" is a proprietary soap-fluid disinfectant, guaranteed Rideal-Walker coefficient 22/24, which was included in order to make the comparison more complete.

Preparation of Disinfectant Fluid Emulsions

The dilutions were prepared by the method described for soap-fluids on page 59 the preliminary 2½% emulsions were agitated for 15 minutes on a mechanical shaker.

Determination of the Disinfectant Value of Phenolic Disinfectants using different Broths

The same broth was used for the broth subcultures, made during each test, as had been employed for the culture of the test organism on the five days previous to the test. The incorporation of two concentrations of Phenol in the tests was found an advantage as it ensured the proper control,

viz., life after 2½ and 5 minutes and no life thereafter. The charts of the tests are shown in Tables XXIII, XXIV, and XXV.

TABLE XXIII

Charts of Rideal-Walker Tests
Broth (a) pH 6.9

Disinfectant.	Dilution	Time culture in contact with Disinf. - mins. 2½ 5-7½ 10	2½ 5 7½ 10	2½ 5 7½ 10
Fluid A	1:800	x - - -		
	1:900	x x - -	- - - -	x - - -
	1:950		x - - -	x x - -
	1:1000	x x x -	x x - -	x x - -
	1:1100	x x x x		
Phenol	1:95	x x - -	x - - -	x x - -
	1:100		x x - -	x x x -
	R.W.Coeff.	9.4	10.0	10.5
Fluid B	1:1500	- - - -		
	1:1600	x - - -	x - - -	x - x -
	1:1700	x x - -	x - - -	x x - -
	1:1800		x x x -	x x x -
Phenol	1:95	x - - -	x - - -	x x - -
	1:100	x x - -	x x - -	x x x -
	R.W.Coeff.	17.0	17.5	18.0
"Cyllin"	1:1600	x - - -		
	1:1700	x x - -	x x - -	
	1:1800	x x - -	x x x -	
	1:1900	x x x -	x x x x	
Phenol	1:95		x x - -	
	1:100	x x - -	x x x -	
	R.W.Coeff.	18.0	17.9	

TABLE XXIV

Charts of Rideal-Walker Tests

Broth (b). pH 7.3

Disinfectant	Dilution	Time culture in contact with Disinf. - mins.											
		2½	5	7½	10	2½	5	7½	10	2½	5	7½	10
Fluid A	1:1100	x	-	-	-	x	x	-	-	x	-	-	-
	1:1200	x	x	-	-	x	x	-	-	x	-	-	-
	1:1300	x	x	x	-	x	x	x	-	x	x	-	-
	1:1400	x	x	x	x								
Phenol	1:100	x	x	-	-	x	x	-	-	x	-	-	-
	1:105					x	x	x	-	x	x	-	-
R.W.Coeff.		12.0				12.0				12.3			
Fluid B	1:1800	x	-	-	-								
	1:1900	x	x	-	-								
	1:2000	x	x	-	-	x	x	-	-				
	1:2100	x	x	x	-	x	x	x	-				
	1:2200					x	x	x	x				
Phenol	1:100	x	x	-	-	x	x	-	-				
	1:105					x	x	x	-				
R.W.Coeff.		20.0				20.0							
"Cyllin"	1:2000	x	-	-	-	x	x	-	-				
	1:2200	x	x	-	-	x	x	x	-				
	1:2400	x	x	x	-	x	x	x	x				
Phenol	1:100	x	-	-	-	x	x	-	-				
	1:105	x	x	-	-	x	x	x	-				
R.W.Coeff.		20.9				20							

TABLE XXV

Charts of Rideal-Walker Tests

Broth (c) pH 7.6

Disinfectant	Dilution	Time culture in contact with Disinf. - mins. $2\frac{1}{2}$ 5 $7\frac{1}{2}$ 10	$2\frac{1}{2}$ 5 $7\frac{1}{2}$ 10	$2\frac{1}{2}$ 5 $7\frac{1}{2}$ 10
Fluid A	1:1200	x - - -		
	1:1300	x x - -	x x - -	
	1:1400	x x - -	x x - -	
	1:1500		x x x x	
Phenol	1:105	x - - -	x - - -	
	1:110	x x x -	x x - -	
	R.W.Coeff.	13.0	12.7	
Fluid B	1:2200	- - - -		
	1:2400	x x - -	x - - -	
	1:2600	x x x -	x x - -	
	1:2800		x x x -	
Phenol	1:105	x x - -	x - - -	
	1:110	x x x -	x x - -	
	R.W.Coeff.	22.9	23.7	
"Cyllin"	1:2400	x x - -	x x - -	x x - -
	1:2500			x x - -
	1:2600	x x x x	x x x -	x x x -
	1:2700			x x x x
	1:2800	x x x x	x x x x	
Phenol	1:105	x - - -	x x - -	x x - -
	1:110	x x x -	x x x -	
	R.W.Coeff.	22.3	22.8	23.2

The results given in the charts are summarised in table XXVI. The phenol coefficients are the mean values of the reported tests, which were made on different dates.

TABLE XXVI

Temperature of medication 17/18°C
Culture - B. Typhosus (Lister), 5th day's 24-hour broth subculture.
Proportion of culture to disinfectant, 0.5 cc. to 5 cc.
Period of incubation, 48 hours. Temperature, 37°C.

Disinfectant tested	Average phenol coefficient of disinfectant		
	Broth (a) pH 6.9	Broth (b) pH 7.3	Broth (c) pH 7.6
Fluid A	10.0	12.0	12.9
Fluid B	17.5	20.0	23.4
"Cyllin" (Medical)	18.0	20.4	22.8
Phenol control dilutions	1:95 and 1:100	1:100 and 1:105	1:105 and 1:110

Further tests with pH 7.6 broths, prepared either by boiling at the neutral point or by omitting this step, have shown no differences in the coefficients of fluids tested with them. The large variations in the results with the above broths cannot therefore be attributed to this factor, although it did seem feasible that the differences might arise from the presence of soaps formed by the saponification of traces of fat derived from the "Lemco". Larson (Proc. Soc. Exp. Biol. Med., 1921/22, 19, 62; Bact. Abs., 9, 252) found that decrease in the surface tension of culture media,

by the addition of soaps, influenced greatly the growth-rate of bacteria, and Wright (J. Bact., 1917, 2, 315) noted that in certain batches of broth which gave abnormally high coefficient values, the ether extractive of the meat extract, on analysis, was 50% greater than usual.

The elevation of the pH value of Rideal-Walker broth from 6.9 to 7.6 increases the amount of insoluble material which is removed during the final filtration. The composition of such insoluble material has been investigated by Wright and found to consist of protein with a considerable amount of phosphate. The decrease in the amount of this material present in the less acid broths may be partly responsible for the increase in the germicidal activity of the disinfectant, either because the bacteria are less protected during the disinfection interval, or on account of the poorer growth of the Typhoid organism owing to the reduced nutritive value of the broth. Additional support is given to these views by the results with broth which had been filtered at pH 8.6 - the boiling point neutrality figure - and then made 1.5% acid, a maximum amount of protein and phosphate being thus removed. The pH value of the broth was 7.1/7.3 and, by its use, the phenol coefficient of fluid B was 25. Similarly the coefficient of fluid C, which was 22 on broth (b), was raised to 25.5. The results show that higher coefficient values have been obtained than

on either the previous pH 7.3 or pH 7.6 broths but the tests were not carried further, as the method of preparation diverged from the conditions of the Rideal-Walker test. Wright reported that the higher coefficient values obtained with such broths were unsatisfactory, particularly in the case of the American Hygienic Laboratory broth, owing to the frequent occurrence of irregularities in the charts. No tests have been conducted to determine the effect of a further decrease in the acidity of the broth, but Wright (ibid) and Kingzett (J.S.C.I., 1906, 25, 1191) have reported tests where reductions in the phenol coefficients were obtained with broths much less acid than pH 7.6.

It would appear from the above tests that the chief factor controlling the coefficients of the disinfectant fluids was the pH value at which the broths were filtered, and used. The decrease in acidity from pH 6.9 to pH 7.6 has resulted in a decrease in the resistance of the test organism, and in an increase of, approximately, one-third in the phenol coefficients. It is possible that the change in the hydrogen-ion concentration alone is sufficient reason for the alteration in the coefficient values, as the rate of growth and vitality of micro-organisms changes with the hydrogen-ion concentration of the media. The results of Schoenholtz & Meyer (Proc. Soc. Exp. Biol. Med., 1919, 16, 151) support such a contention in the present instance, as they determine that the optimum generation time of B.

Typhosus occurs at pH 6.8 to 7.0.

Wright (ibid) found, when using American Hygienic Laboratory broth, that the phenol coefficient value of a disinfectant fluid increased as the acidity of the broth increased from pH 6.0, was constant between pH 6.0 and pH 7.0, and decreased as the acidity of the broth decreased from pH 7.0. The difference between this last result and the author's results on the pH range from 6.9 to 7.6 may be accounted for by differences in the proportion of the ingredients of the two broths, particularly by the salt content, and in the proportion of the broth-culture of the test-organism to the disinfectant. Rideal-Walker broth contains a greater amount of "Lemco", peptone, and salt, and the technique of the test includes the introduction into the disinfectant and phenol dilutions of a larger quantity of the broth culture of the test organism. This latter factor may be extremely important, as the salt and organic matter introduced with the broth will affect the surface concentration of the phenol and the disinfectant at the bacterial interfacial surface. (cf. Rideal, Fifth Report on Colloid Chem." H.M. Stat. Off., 1923, 31)

S. Rideal and E. K. Rideal ("Chem. Disinf. and Sterilis" p. 294), while discussing the factors requiring more careful specification for an international test, mention that the present method of standardising the broth is unsatisfactory, and suggest replacing it by a direct adjustment of the broth

to a definite pH value. The reaction of pure water pH 7.0 is suggested by them, and would seem particularly favourable, as Schoenholtz & Meyer have determined that the optimum generation time of B. Typhosus occurs at pH 6.8/7.0.

These results were reported in a paper by the author (J.S.C.I., 1926, 45, 472), and it was finally mentioned that the adjustment of the broth to pH 7.0, if adopted without further alterations in the test, would effect a reduction in the presently accepted Rideal-Walker coefficient values.

Revised Method of Standardising Rideal-Walker Broth.

The author is indebted to S. and E. K. Rideal and A. Sciver for their reply. (J.S.C.I., 1927, 46, 152). They condemn the boiling-point titration and the dilution of the media previous to titration, and introduce a revised method of standardising the broth. The following excerpts are from their letter:-

"While recognising that the results obtained with broth "standardised by different methods are of some theoretical "scientific interest, we cannot help feeling that there "have been many attempts in the past to create difficulties "where they do not exist. In fact we can see no incontest-"able reason for neutralising the broth at the boiling point "using phenolphthalein, and we maintain that it is quite "incorrect on general scientific grounds to dilute the broth "before titration."

"Apparently Mr. Moore agrees that an indicator method "is preferable. In actual practice, of course, phenol- "phthalein is used and the neutralisation is effected cold. "The reaction of such a broth is pH 7.6, a value in good "agreement with that calculated from the limiting conditions "of phenolphthalein and the salt effect, i.e.

$$7.80 - 0.16 = 7.64$$

"We have been using such a medium for many years."

"Mr. Moore's positive recommendation appears to be to "alter the pH from 7.6 to 7.0. This could readily be done, "of course, by using some other indicator, but Mr. Moore "apparently forgets that by doing so we should be rendering "an enormous amount of work incomparable without any obvious "gain in other directions.

The following reply was made by the author (J.S.C.I., 1927, 46, 196) to the editor of the journal:-

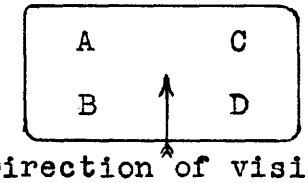
"Sir, - I feel obliged to Messrs. S. and E. K. Rideal "and A. Sciver for their letter in your issue of Feb. 18, since "it definitely establishes pH 7.6 as the reaction value of "Rideal-Walker broth. The main purpose in writing my paper "was to draw attention to the effect of differences in the "reaction of the broth and to show the necessity for fixing "the reaction at some definite value, but I do not think "that the wording of my paper can be interpreted as making a "positive recommendation for the reduction of the pH value "to 7.0.

"I favour the new method of standardising the broth as "outlined in their letter, particularly if the titration is "conducted with the aid of a comparator and the colour of "the indicator is controlled by a standard buffer solution. "It may be noted, however, that this method of standardising "the broth to pH 7.6, by direct neutralisation to phenol-"phthalein, differs from the published technique by omitting "the after addition of 1.5% normal hydrochloric acid; this "alteration may be responsible, in part, for the discrepan-"cies in the reported results of different operators."

The reason for insisting on the use of a comparator, and standard buffer solution control, depended on the observance that no colour was obtained in a pH 7.8 sodium phosphate buffer solution until saturated with phenolphthalein. Kolthoff ("Indicators" trans. Furman, London, 1926, 81) gives the transition interval of phenolphthalein as from pH 7.8 to pH 9.4, provided the solution is saturated with phenolphthalein; with decreasing concentration the colour change is effected at higher pH values. The solubility of phenolphthalein is further given as 8 c.c. of a 1% solution per litre, which is equivalent to 0.08 c.c. of a $\frac{1}{8}$% solution in 5 c.c. The concentration used was 0.1 c.c. of a $\frac{1}{2}$% alcoholic solution of phenolphthalein per 5 c.c. buffer solution.

The following new procedure was adopted for standardising the broth:-

The broth, after solution of the ingredients and filtration, was cooled and to an aliquot portion, 5 c.c., was added 0.1 c.c. of a ½% alcoholic phenolphthalein solution. The titration with 0.1N- sodium hydroxide was conducted in a comparator, as set out below.



Direction of vision

A = 5 cc pH 7.8 sod. phos. buffer soln. plus 0.1 cc. ½% phenolphthalein soln.

C = 5 cc pH 7.8 sod. phos. buffer soln.

B = 5 cc. Broth

D = 5 cc broth plus 0.1 cc ½% phenolphthalein soln.

The broth tubes were diluted equally with 0.1N-NaOH as the titration proceeded, and the concentration of the indicator was maintained in broth tube (D) by the intermittent addition of fresh indicator as the volume increased. The volume of 0.1N- sodium hydroxide was noted which it was found necessary to add to tube (D) in order to obtain the same colour in the right-hand pair of tubes, as was observed in the left-hand pair. From this reading the volume of N-sodium hydroxide required to neutralise the remainder of the broth was calculated, and, after addition, the accuracy of the neutralisation was checked in the comparator.

The electrometric pH value of broth standardised by the above method was 7.60 and 7.63, on separate occasions.

The colorimetric pH value by Clark and Lub's method, using Phenol Red as indicator, was 7.7. The phenol coefficient of "Medical Cyllin" was 22/24, as guaranteed. The tests were as follows:-

Disinfectant	Dilution	Time culture in contact with disinf. - mins.							
		2½	5	7½	10	2½	5	7½	10
"Cyllin" (Medical)	1:1800	x	-	-	-	x	x	-	-
	1:2000	x	-	x	-	x	x	-	-
	1:2200	x	x	-	-	x	x	-	-
	1:2400	x	x	x	-	x	x	x	-
	1:2600					x	x	x	x
Phenol	1:95					x	x	-	-
	1:100	x	x	x	-				
R.W.Coeff.			24.0				23.2		

This method of standardising the broth was used in all subsequent tests.

PART IV

COMPARISON OF THE DATA OBTAINED FROM THE FIELDS WITH DIFFERENT SOURCES OF ERR

The Proportions of the Phenols in Tars.

The proportions and type of the phenols is dependent primarily on the material carbonised, viz., coal, shale, wood, etc. The nature of the coal, and in particular the amount of Oxygen present, is said by Parrish (Fuel, 1926, 456) to be the chief factor governing the amount of phenols in coal-tar but, in addition, the temperature of carbonisation influences the yield. A temperature of 500° has been found by Broche to correspond with a maximum yield of phenols. Increase in the temperature of carbonisation decreases the yield of phenols and alters their chemical structure. Because of this change in chemical structure, which is not confined to the phenolic constituents alone, tars are classified as products of low temperature or high temperature carbonisation.

Low temperature tars are found to contain a large proportion of high boiling viscous phenols, resinous in character, together with many of the homologues of phenol. High temperature tars, by comparison, are composed almost entirely of the lower true phenol homologues:- phenol, cresol, xylenol. The phenols may comprise up to 50% of L.T. tar (Parrish, ibid) but represent only 5/10% of H.T. tar. Comparison of the distilling points of the phenols from a number of tars is given in table XXVIa, prepared from data of Macleod, Chapman, and Wilson. (J.S.C.I., 1926, 45, 401T). These results show that high temperature tars are normally deficient in

high boiling acids and explain why, before the introduction of vertical retorts and low temperature carbonisation plants, the main supply of high boiling tar acids for disinfectant manufacture was obtained from blast-furnace tar oils, which were produced under lower temperature conditions than those of horizontal gas retort practice. The blast-furnace oils represent about 33% of the tar and contain from 25% to 35% of phenols distilling between 205°C and 360°C.

TABLE XXVIa

Producer	Glasgow Corpn. Dalmarnock	Glasgow Corpn. Provan	Glasgow Corpn. Tradeston	South Metropolitan	J. Nimmo & Co. Ltd. Auchengeich
Type of retort	MacLaurin low temp.	Vertical	Horizontal (High heats)	Horizontal	Coke Oven (ultra narrow)
Average temp. °C	600/700	1000/1200	900/1200	900/1200	1300
Coal used	Lanarkshire gas	Lanarkshire gas	Lanarkshire gas	Durham & foreign	Auchengeich colliery
Yield of tar, gls/ton coal	16.5	14.8	10.8		6.0
Sp.Gr.Tar	1.050	1.075	1.212	1.156	1.264
Crude phenols, gls/ton tar	41.0	18.72	6.95	5.74	0.14
Do., % by vol. of tar	19.3	9.0	3.76	2.96	0.08
Temp. °C	Distillation range of refined phenols				
190	-	-	-	3	-
195	-	-	4	8	4
200	3.5	4	31	37	6
210	24	38	71	74	28
220	50	57	84	88	54
230	65	70	90	94	66
240	75	75	94	-	71
260	85	83	-	-	79
280	92	90	-	-	86
300	-	-	-	-	90

Choice of Tars for Examination.

It was decided that the separation and examination of the lower boiling phenols, viz., phenol and cresol, would be of little advantage, since this ground had already been covered both by the chemist and the bacteriologist. Very little is known however, about the phenols distilling above 240°C, which is beyond the range of the xylenols and trimethylphenols, and it was determined to concentrate on these higher fractions since knowledge of the disinfecting value might assist in elucidating their chemical structure. The choice of tars had to include both high and low temperature carbonisation products, but it was not considered essential to commence from the tar itself where a commercial distilled oil was available. The following products were chosen for examination:-

High temperature tar products.

(1) Coke-oven creosote oil.
(2) "Tradeston" heavy creosote oil.

Low temperature tar products.

(3) Blast-furnace creosote oil.
(4) "MacLaurin" low temperature tar.
(5) Phenols extracted from shale oil.

The following particulars are known regarding these oils:-

(1) This oil was distilled by Messrs. Wm. Baird & Co. Ltd., from their coke-oven tar at Bedley Works. The oil is an average sample of the portion of the distillate which is treated for the recovery of tar acids and naphthalene,

and represents about 55% of the total oil distilled from the tar. The tar is normally distilled to pitch (medium soft quality), and the total oil (S.G. 1.035 @ 60°F) ranges from 37% to 40% of the tar.

(2) Two gallons of this oil were kindly given the author by Mr. Macleod, manager of Glasgow Corporation Chemical Works Department. Data published by Macleod, Chapman and Wilson (J.S.C.I., 1926, 401T) mention that Tradeston works produce only horizontal retort tar and the yield of heavy oil is given as 1.6 gallons per ton of coal, equal to 14.8% by volume of the tar. The following information relative to this sample, was supplied:-

Sp.Gr. (60°F) 1.059. Tar acids 9%
Distillation test (Volume taken 300 c.c.)

1.	(- 170°C	=	2 c.c.	=	0.66%
	(170 - 270 "		178 "		59.3%
2.	(270 - 300°C	=	45 c.c.	=	15%
	(300 - 360 "		58 "	=	19.3%
	Residue (difference)				5.74%
	Naphthalene in 1.		84 gms.	=	28%
	Anthracene " 2.		16 "	=	5.3%
	Tar acids in 1.			=	3%
	" " " 2.			=	6%

(3) The blast-furnace creosote oil was obtained from Messrs. Wm. Baird & Co. Ltd., and is their own manufacture. It is the standard commercial oil.

(4) This sample of MacLaurin tar was obtained from the

Glasgow Corporation Chemical Works Department and the tar had been centrifuged in order to reduce the percentage of water.

(5) The shale-oil phenols were supplied by Professor T. Gray, director of the Scottish Shale Oil Research Assoc. The crude phenols were extracted from topped Shale Oil, i.e., the residual oil after the petrol fraction has been distilled off in continuous stills. The shale oil was washed with 60° Tw-sodium hydroxide, the resulting sodium phenate was separated and decomposed with dilute sulphuric acid. The crude phenols were distilled and gave a yield of refined phenols amounting to about 1% of the topped oil.

Distillation of MacLaurin Tar.

Before proceeding with the extraction of the phenols from this tar, it was first necessary to distil the tar and obtain a product comparable with the other oils. A preliminary distillation of 100 c.c. of the tar was made in order to determine the prominent features of the tar and estimate how far the distillation should be carried. This distillation proceeded smoothly, the tar did not froth excessively during the removal of water and there were no signs of heavy decomposition towards the end of the distillation. The result indicated that 60% by weight of the tar could be distilled off without either coking the pitch, or leaving too soft a pitch.

4000 gms. of the tar were distilled from a 3 litre upright cylindrical iron still, which was provided with an adjustable ring burner fitting round the outer circumference. The ring burner, at the start of the distillation, was just below the level of the tar in the still and was gradually lowered during the progress of the water distillation until, when all the water was over, the burner was almost level with the bottom of the still. The following are the details of the distillation, the temperatures recorded are corrected for errors of the thermometer, the exposed emergent stem, and barometric pressure.

Distillation MacLaurin Tar - 4000 gms.

Temperature °C (corr.)		% by wt.	% by vol.	Rate c.c./min.
Water		3.9	4.06	
Oil distillate @	150	0.11		
	160	0.16		
	170	0.25	0.26	
	180	0.35		3
	190	0.7		
	200	1.2		
	210	4.2	4.7	4
	220	9.5		
	230	14.0		5
	240	18.5	20.2	
	250	22.7		6
	260	30.2		
	270	32.1	34.3	6.5
	280	36.5		
	290	41.0		
	300	45.4	48.4	7
	310	50.9		
	322	57.9	61.5	
Pitch		35.0)		
Coke in still and loss		3.2)	34.4	

The light oil which distilled over with the water was separated, and returned to the still. The distillation was stopped at 210°C in order to replace the water-condenser with an air-condenser. The rate of distillation was increased after 210°, but even with the increased rate of distillation cracking was made apparent from 250° upwards by the presence of water globules in the distillate. At 290°, a yellow deposit resembling milk of sulphur formed on the upper surface of the condenser tube. 322° was the maximum temperature observed and the distillation was then stopped, as the temperature was falling rapidly owing to decomposition. The pitch was "medium soft" grade; the M.P. was 74°C (Kraemer and Sarnow's method) and the twist point 125°F.

Physical Tests of the Oils.

Specific Gravity (60°F):- This constant was determined by means of the Westphal balance, the temperature of the oil being adjusted to 15.5°C.

Tar Acids:- The approximate percentage of tar acids present was determined from the contraction in volume of the oil when 20 parts of the oil were shaken with 80 parts 9%-NaOH solution. Higher results are obtained with stronger sodium hydroxide solutions but these generally are more inaccurate owing to the occlusion of oil by the phenate. The difference in results when 9% and 18% sodium hydroxide

solutions were used is shown in table XXVIb. The percentage tar acids in the latter test was determined from the contraction in volume of the oil when equal volumes of oil and 18%-NaOH were mixed. The results of the extraction of the phenols in quantity from the oils is also given in table XXVIb and it is observed that these figures compare very favourably with the 9%-NaOH test, when allowance is made for the amount of water present in the oil.

Distillation Test:- A 100 c.c. sample of the oil was distilled from a 200 c.c. Jena distillation flask, which was surrounded by an asbestos box. The box had a 2 inch circular serrated hole in the centre of the base, over which the flask rested, and a 1 inch circular hole in the top cover through which the neck of the flask just projected. A slot cut halfway down the centre of one side permitted the flask to be set upright within the box with the side-tube directed downwards. The thermometer was held in position in the neck of the flask by a cork, the top of the bulb of the thermometer being in line with the bottom of the side outlet tube. The thermometers, in use, were compared against a 360°C standard thermometer, and all observations were corrected for the thermometer error before being recorded as observed temperatures. Corrected temperature readings were obtained after allowance had been made for errors caused by the cold emergent stem of the thermometer and by variation from normal barometric pressure. The formulae

given by Young ("Distillation Principles and Processes" London, 1922, p.11) were used for calculating the corrections. The rate of distillation was adjusted to 3 c.c. per minute.

TABLE XXVIb

Physical Tests of Oils

Name	Coke-oven creosote	Tradeston heavy oil	Blast-furnace creosote	MacLaurin L.T.Distd. oil	Shale-Oil phenols
Sp.Gr.15.5°C.	1.012	1.057	0.9744	0.9841	0.9705
% Tar acids- 9% NaOH	17	9	26	33	50
% " " -18% "	20	10	33	40	60
% " " by extr.	16.4	8.5	25.6	30.5	48.5
Distillation Test					
Water	0.6%	Trace	0.7%		1.2%
I.P. °C (corr.)	98°C	185°C	195°C		88°C
Distd. oil @ 190° "	8%				2.5%
200	24				5.0
210	40	2%	1.5%		9
220	52	6	7.0		16
230	63	11	19.5		25
240	70	30	33.0		34.5
260	81	48	49.5		45
280	86	59	65.0		54.5
300	90	66.5	76		62
320	92.5	73.5	84.5		70
340	-	84	90		78
360	-	90.5	95.0		89

Washing of Oils with Sodium Hydroxide and recovery of Crude Phenols

The use of very strong sodium hydroxide solution, e.g. 60°Tw, for washing the oil is not found advantageous in practice, since the hydrocarbon oils occluded by the phenate, increase abnormally, and the usual procedure is to employ 20°Tw-sodium hydroxide. Several workers have found, however, that some of the phenol homologues are not extracted by sodium hydroxide of this strength. Morgan and Meighan (J.I.E.C., 1925, 17, 626) found that complete extraction of coke-oven oil was obtained only with 19%-NaOH, or stronger, when using the calculated equivalent amount of sodium hydroxide, and in experiments with hydrogas L.T. tar oil an optimum extraction was obtained with 23.5%-NaOH. Greenbaum (Catalyst, 1927, 12, 6; Amer. C. Abs., 1927, 2975) similarly obtained an optimum extraction of a L.T. tar fraction containing 28% phenols with 15%-NaOH and the first wash removed over 90% of the phenols present. The increased extraction with stronger sodium hydroxide is due to the increased solubility of the free phenols in the concentrated sodium phenate. L.T. tar phenols are said by Morgan and Meighan to be inextractable with sodium hydroxide, since they are less acidic in character and their salts are largely hydrolysed in solution, causing equilibrium to be reached before extraction is completed.

In the present work it was decided to first fully

extract the oil with 9%-NaOH, and to continue the washing with 18%-NaOH, as required. The amount of 9%-NaOH used was approximately four times the volume of phenols present, which was about 25% in excess of requirements. The sodium hydroxide was added to the oil in two washes, 60% with the first wash; this procedure was adopted in order that ample excess would be present in the final wash. The oil and sodium hydroxide were heated to 50/60°C before mixing. The weak and strong phenates were kept separate, the hydrocarbons removed by washing with 15% Benzol in two portions, and the washed phenate boiled for 20 minutes to remove benzol and traces of pyridine. The two phenates were now mixed, and decomposed with 10%-sulphuric acid. The crude acids were separated and the sodium sulphate solution extracted with pure benzene, which was found to be a better solvent than methylated ether for the recovery of the phenols. The charts, tables XXVII to XXXI, give full details of the process of washing the oils and recovering the phenols, with the yields of the products.

By the above system of washing, complete extraction of the phenols from the oils was not obtained with 9%-NaOH. Subsequent washing with 18%-NaOH successfully removed the remainder of the phenols from high temperature tar oils but was the cause of emulsion formation with low temperature tar oils. These emulsions were only successfully broken down by dilution with methylated ether and water. This emulsion

formation might be prevented by extraction of the oils with 18%-NaOH alone, as the emulsifying bodies would possibly be soluble in the larger volume of strong sodium phenate. Edwards (J.S.C.I., 1924, 43, 144T) used only 13.5%-NaOH for washing blast-furnace, MacLaurin, and coalite L.T. tar oils, and obtained complete extraction of the phenols.

The extraction of L.T. tar phenates with Benzol, or methylated ether, removed in part phenolic bodies which were in solution in the sodium phenate. The phenolic substances thus removed were not soluble in 18%-NaOH, but formed an emulsion layer between the oil and the sodium hydroxide similar to the emulsions formed during the washing of the oil. Phenolic substances which are soluble in sodium phenate but not in sodium hydroxide, have been reported by other authors to be removed by extraction with certain solvents. Weindal (Brennstoff. Chem., 1925, 6, 217, 234) has thus separated low temperature tar phenols into two fractions, viz., "e-phenols" which are extractable from sodium phenolate liquor with ether or benzene, and "ne-phenols" which are not extractable but are recovered from the water solution by precipitation with mineral acids. The "e-phenols" represent 47.2% of the phenol fraction B.P. 230/310° C from rotary tar, are more complex and unstable, and on distillation decompose largely yielding humic acids and asphalt-like matter. The results of the solvent extraction of low temperature

tars at the Chemical Research Laboratory, Teddington, which were reported by G. T. Morgan, (J.S.C.I., 1928, 47, 131T) subsequent to the completion of the work for this thesis, bear directly on the above problem, and I take the opportunity of quoting from this paper.

"One of the distinctive features of low temperature "tar is the high percentage of material extracted by dilute "aqueous caustic soda. This extractable portion varies be- "tween 25% and 33% of the tar.

"It has, however, long been recognised that the alkaline "solutions of phenols dissolve also amorphous materials "which are non-phenolic in character. Some of these pro- "ducts slowly settle out from the alkaline solution, and "others are extracted from this solution by means of organic "solvents.

"The presence of these non-phenolic materials - the "solids have been termed ulmins - in the alkali extract of "the tar is due to the solvent action of aqueous sodium "phenate or sodium phenoxide.

"An alkaline solution of low temperature tar will render "soluble 33% of the total tar, but on treating this solution "with chloroform a viscid mass is precipitated amounting to "6% of the tar, whereas the chloroform dissolves phenate "soluble materials corresponding with 13% of the tar, leaving "dissolved in the alkaline solution about 13% of true "phenols.

"The phenate soluble constituents precipitated by salt "or removed by chloroform are now quite insoluble in aqueous "caustic soda."

The products removed by the benzol washing of L.T. tar phenates in the present experiments are similar in certain respects to the phenate soluble constituents reported by G. T. Morgan but are not completely insoluble in aqueous caustic soda. They are nearer true phenols and resemble the L. T. tar phenols of Morgan and Meighan, which are said to be hydrolysed largely in solution and, therefore, are only extractable with sodium phenate. Allowance has been made for these phenate soluble phenols when determining the total yield of phenols, as given in the final tables analysing the washing of MacLaurin L.T. tar and shale-oil crude phenols in the charts, pages 154 and 155.

The washed oils, or neutral oils, were free from phenols in every case and the physical tests of the oils are given in the following table:-

Physical Tests of the Neutral Oils

Name	Coke oven creosote	Tradeston heavy oil	Blast-furnace creosote	MacLaurin L.T. oil	Shale oil
Sp.Gr.15.5°C	0.998	1.054	0.9476	0.9465	0.899
Distillation Test					
Water	Nil	Nil	0.1%	Trace	Nil
I.P. °C (Corr.)	122	176	197	170	158
Distd.oil @ 190°C "	7.6%			1.5%	2.0%
200 "	15.5			5.5	5
210 "	27.5			9.0	8
220 "	38	2.0%	2.0%	13.5	12
230 "	50.5	7	6.	20	17
240 "	61	20	11	25.5	22.5
260 "	76	44	31	38	32.5
280 "	85	55	54	50	44
300 "	91	64.5	69	62	55
320 "		74	80.5	73	65.5
340 "		82	87.5	81.5	75
360 "		90	94.0	91.5	86.5

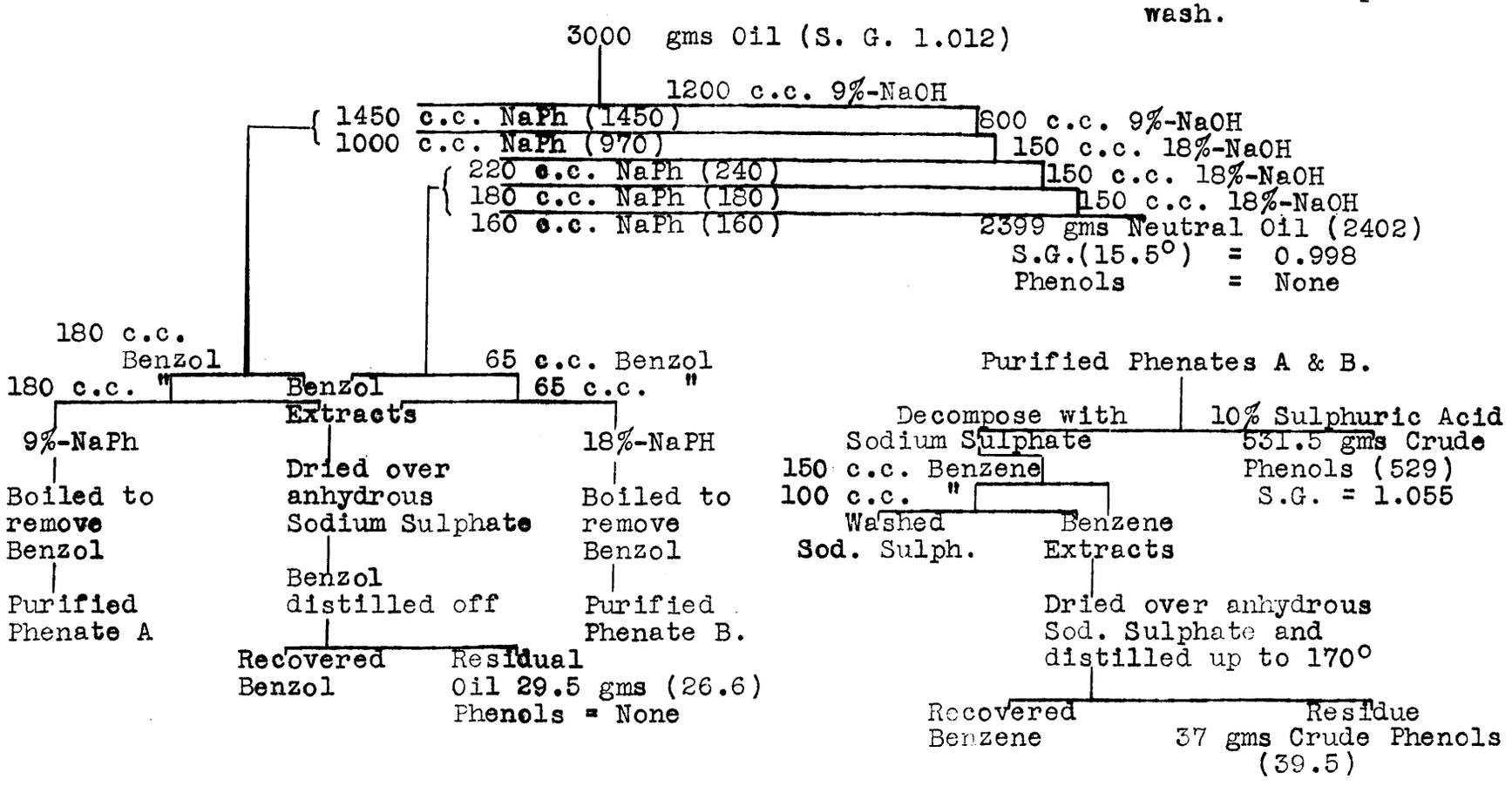
TABLE XXVII

WASHING CHART FOR COKE OVEN CREOSOTE OIL

COKE OVEN CREOSOTE OIL

Washing Chart

Note:- Figures in brackets refer to a duplicate wash.



Analysis of Washes (2) of 6,000 gms. oil

			% by Wt.	% by Vol.
Neutral Oils separated	4801 gms			
" " recovered from phenates	56 gms	4857 gms	80.95	82.1
Crude Phenols separated	1060.5 gms			
" " recovered from sulphate	76.5 "	1136.5 "		
Water present in Crude Phenols		105 "		
Dehydrated Crude Phenols		1031.5 "	17.2	16.4
Water present in Crude Oil			0.6	0.6
Washing Loss			1.25	0.9
			100	100

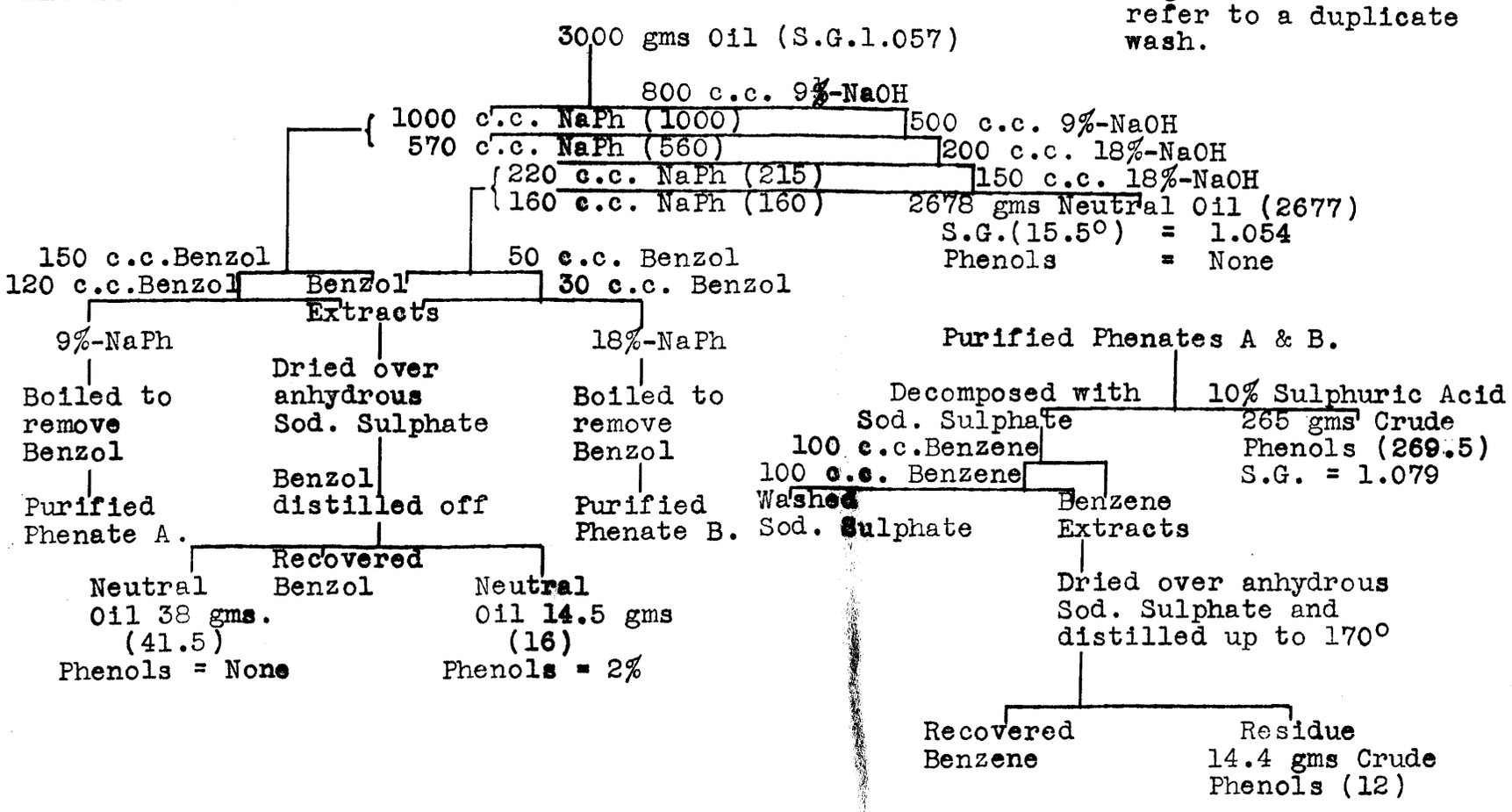
TABLE XXVIII

WASHING CHART FOR TRADESTON HEAVY OIL

TRADESTON HEAVY OIL

Washing Chart

Note:- Figures in brackets refer to a duplicate wash.



Analysis of Washes (2) of 6,000 gms. oil

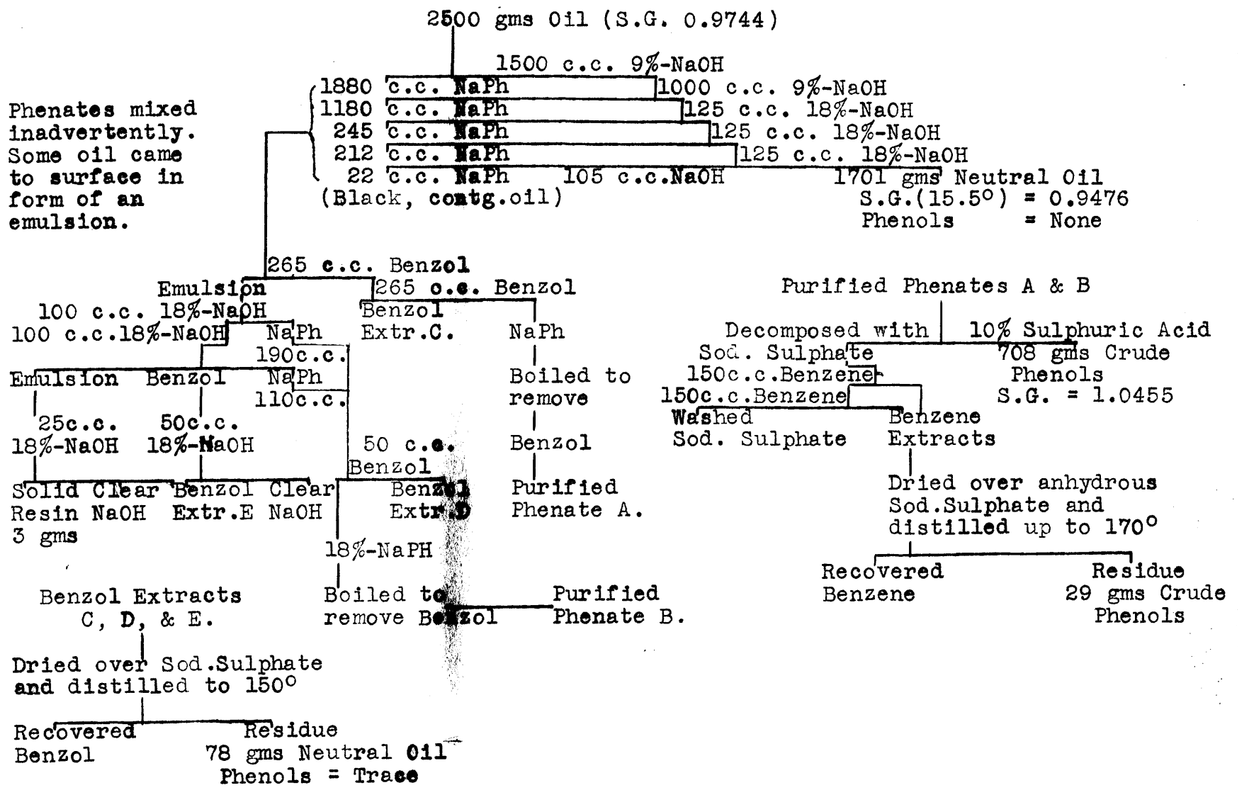
			% by Wt.	% by Vol.
Neutral Oils separated	5355 gms	5465 gms	91.1	91.2
" " recovered from phenates	110 "			
Crude Phenols separated	534.5"	561 "		
" " recovered from sulphate	26.5"			
Water present in Crude Phenols		43 "		
Dehydrated Crude Phenols		518 "	8.6	8.5
Washing Loss			0.3	0.3
			100	100

TABLE XXIX

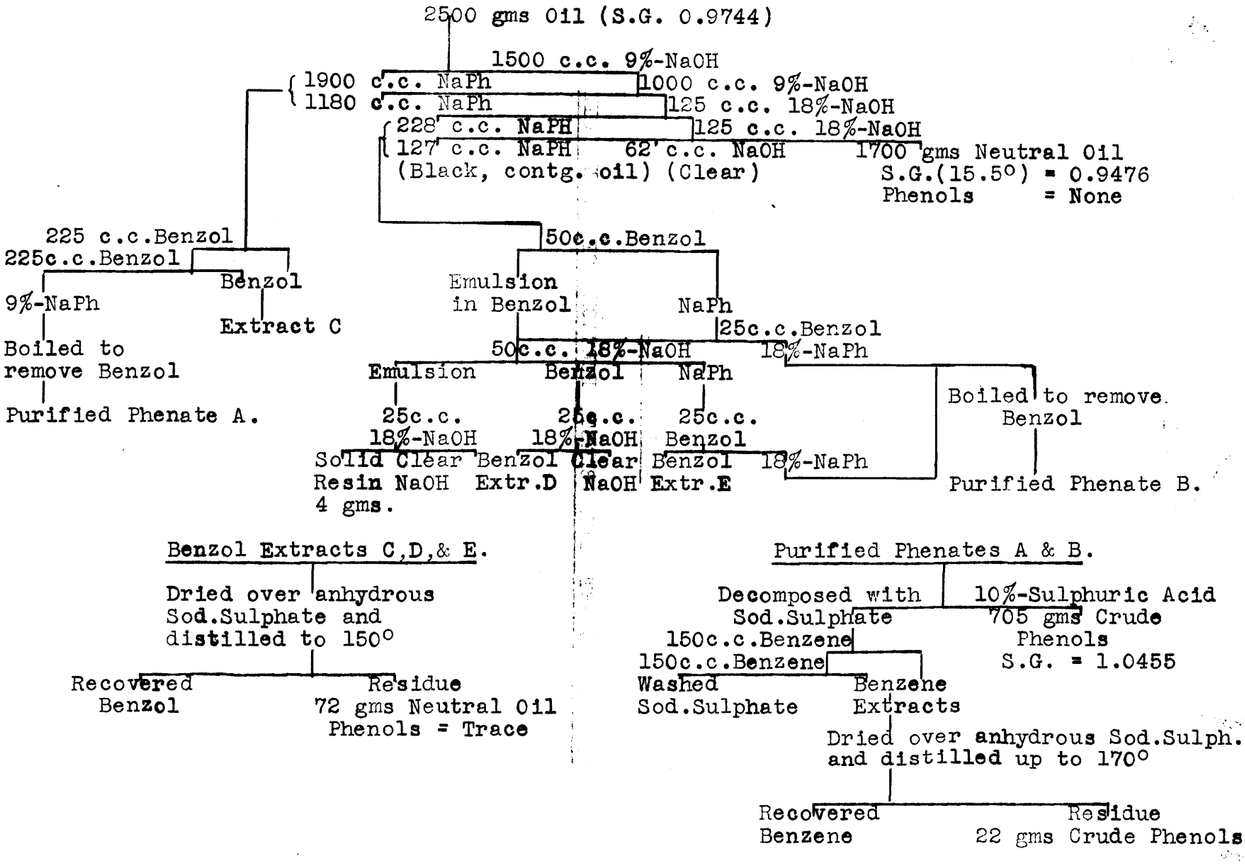
WASHING CHART FOR SMART [illegible] CREOSOTE OIL

BLAST FURNACE CREOSOTE OIL

Washing Chart No. I



Washing Chart No. II.



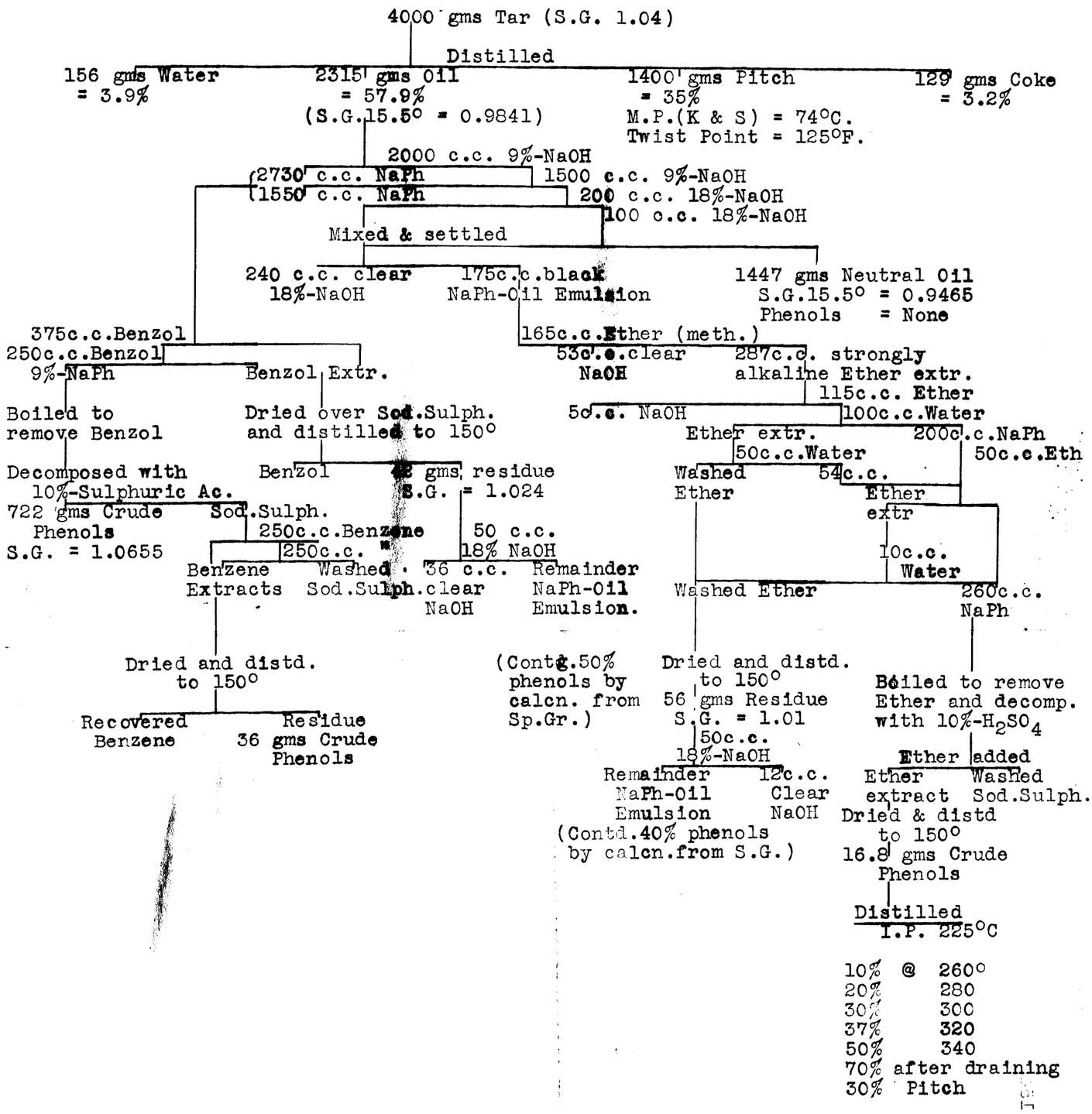
Analysis of Washes (2) of 5,000 gms. oil

			% by Wt.	% by Vol.
Neutral Oils separated	3401 gms			
" " recovered from phenates	150 "	3558 gms	71.2	73.1
Solid resins	7 "			
Crude Phenols separated	1413 gms			
" " recovered from sulphate	51 "	1464 "		
Water present in Crude Phenols		90 "		
Dehydrated Crude Phenols		1374 "	27.5	25.6
Water present in Crude Oil			0.7	0.7
Washing Loss			0.6	0.6
			100	100

TABLE XXX

WASHING CHART FOR MACLAURIN LOW TEMPERATURE TAR

Washing Chart



Analysis of Wash of 2315 gms. oil

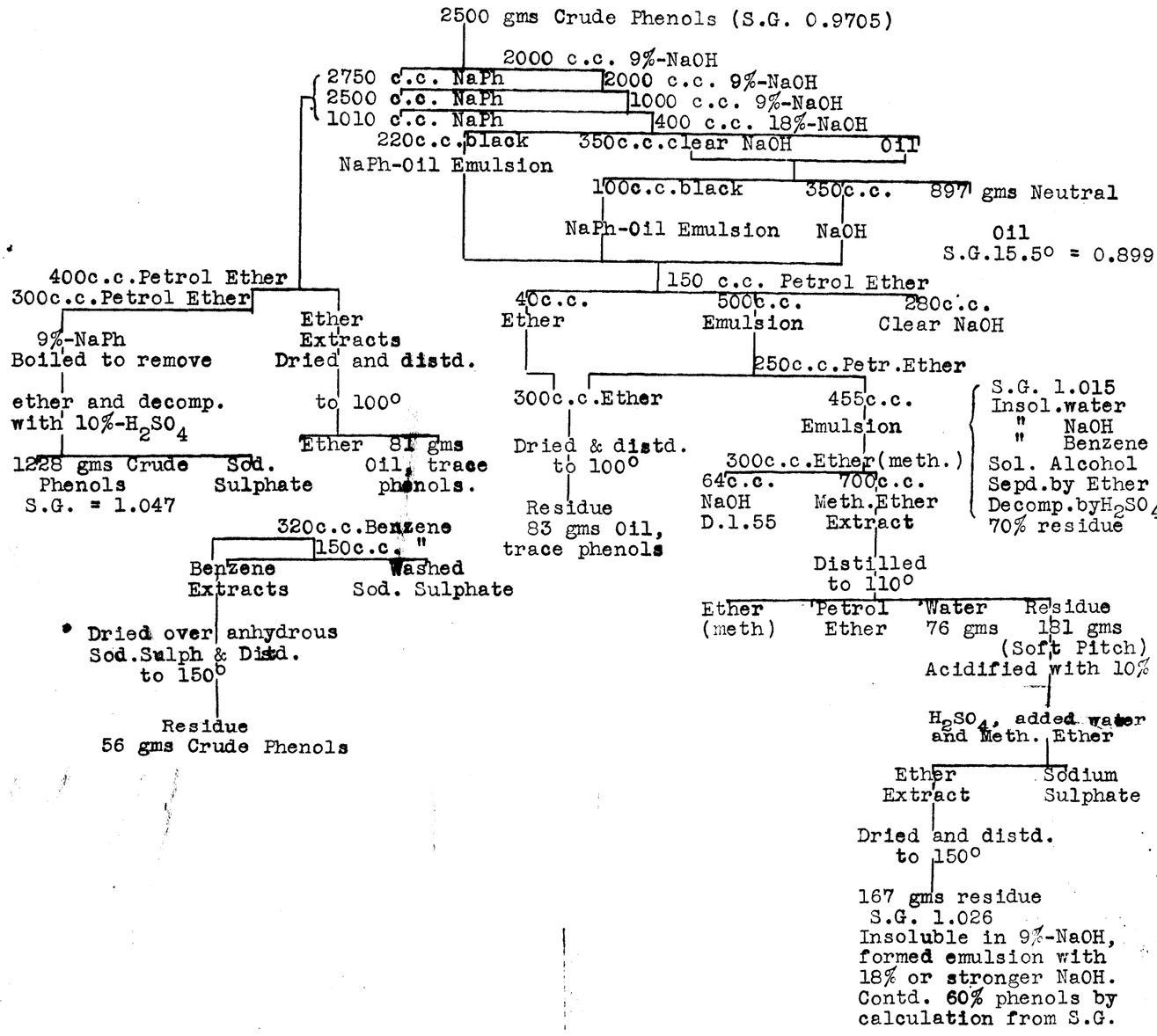
		Oil		Tar
		% by Wt.	% by Vol.	% by wt
Neutral Oil separated	1447 gms			
" " present in Benzol Extr.of 9%-NaPh	21 "	1502 gms 65.0	67.4	37.55
" " " " Ether " " 18%-NaPh	34 "			
Crude Phenols separated	722 "			
" " recovered from sulphate	36 "			
" " " " 18%-NaPh	17 "	818 gms		
" " present in Benzol Extr.of 9%-NaPh	21 "			
" " " " Ether " " 18%-NaPh	22 "			
Water present in Crude Phenols	60 "			
Dehydrated Crude Phenols	758 "	32.8	30.5	18.95
Washing Loss (including water formed by decomposition during distillation of the tar)		2.2	2.1	1.4
		100	100	57.9

TABLE XXXI

MARKING CHART FOR SHALE OIL PHENOLS

SHALE OIL CRUDE PHENOLS

Washing Chart



Analysis of Wash of 2500 gms. crude Phenols

			% by Wt.	% by Vol.
Neutral Oil separated	897 gms.			
" " recovered from 9%-NaPh	81 "			
" " " " 18%-NaPh emulsion	83 "	1128 gms	45.1	48.6
" " present in residue " "	67 "			
Crude Phenols separated	1228 "			
" " recovered from sulphate	56 "			
" " present in residue from 18%-NaPh emulsion	100 "	1384 "		
Water present in Crude Phenols		70 "		
Dehydrated Crude Phenols		1314 "	52.6	48.5
Water present in Crude Oil			1.2	1.2
Washing Loss			1.1	1.7
			100	100

Distillation of the Crude Phenols

The crude phenols, after separation from the sodium sulphate solution, were collected in a large separating funnel and settled for several days. The phenols were warmed during the daytime by immersing the funnel in hot water, as an additional aid to settling. Removal of all the water by solution of the phenols in a solvent was not attempted, as this method departs from practical procedure and, in addition, causes the separation of the phenolic bodies into groups such as true phenols, rhetinols or phenolic asphalts, and acid resins or ulmins, in accordance with the solvent employed (Parrish, Fuel, 1926, 5, 436/465).

The crude phenols were distilled from a 1 litre Jena distilling flask, enclosed by an asbestos box and connected to an air condenser. The phenols were weighed into the flask, the quantity distilled varying between 500 c.c. and 700 c.c. The distillation was stopped after all the water had distilled over and the steam distilled phenols were returned to the flask. The distillation was restarted and the volume which had distilled at definite temperatures was noted; corrections were made at the time to the observed temperatures to convert them to corrected temperature readings.

The distillate was cut into fractions distilling between the following corrected temperatures:- below 210°C; 210/240°C; 240/270°C; 270/310°C; above 310°C. The

distillation was not stopped at these cutting points, in order to drain the condenser tube, but the tube was flamed with a bunsen previous to the change over of receivers. Draining the condenser tube would not have increased the distillate by ½%, but would certainly have increased cracking. The rate of distillation in all cases was 2.5/3.0 c.c. per minute up to 270°C, and from 270° upwards was 3.0/4.0 c.c. per minute. An increased rate was made possible with the higher boiling phenols and assisted in reducing cracking. The end-point of the distillation was reached when the temperature was observed to drop several degrees, as the result of rapid decomposition. The flask was cooled and weighed, in order to determine the weight of pitch, and the pitch then dissolved out with hot cresylic acid. The pitch was not coked in any of the distillations and the same flask was used on every occasion.

The cutting of the distillate into fractions during the crude distillation was decided upon for two reasons:-

(1) In order to prevent additional cracking of the phenols by redistillation.

(2) Because it was known from experience in practice that from 220°C upwards the fractional distillates from column fractionated and straight distilled high boiling tar acids were scarcely distinguishable from one another physically, and the quantities did not differ to any extent.

The cutting-points were chosen in order to concentrate known phenols in certain fractions and eliminate them from

others, e.g., below 210° cresols; 210/240° xylenols; 240/270° tetramethylphenols and other complex mononuclear phenols; 270/310° naphthols and derivatives; above 310°C anthranols and polycyclic phenols. A further reason for the 310° cutting-point was to prevent the inclusion in the previous fraction of decomposition products formed at the finish of the distillation.

The results of the distillations are shown in tables XXXII to XXXIV. In all the distillations there was a noticeable change in the viscosity of the phenols from 270° upwards. Slight decomposition commenced from about this temperature and was made apparent by the formation of a mist of small water globules in the condenser. The colour of the MacLaurin phenols differed from the others; up to a temperature of 240° they were very green, then they changed to the normal reddish-brown but finished a vivid crimson.

TABLE XXXII

Distillation of crude phenols

Source of phenols	Coke-oven creosote oil		Tradeston heavy oil	B.F. creosote oil		MacLaurin L.T.tar oil	Shale Oil	
	I	II		I	II		I	II
Sp.Gr.15.5°C	1.0555		1.079	1.0455		1.0655	1.047	
Vol.distd.cc.	500	577	517.4	700	690	708	610	610
I.P. °C (corr)	178	179	192	194	194	178	204	203
End-point "	233	235	345	322	325	334	358	357
Water % by vol.	9.9	9.65	8.3	6.5	6.5	8.55	5.7	5.7
Phenols % "								
at 190°C (corr)	0.8	0.7						
195	9.2	7.0						
200	31.0	35.4	1.5			0.55		
205	59.4	57.5	10.8	2.8	1.5	4.9		
210	69.3	68.0	25.8	6.8	7.2	22.6	1.7	0.8
215	75.5	75.1	36.2	20.1	20.6	30.8	4.6	5.7
220	78.6	78.1	41.8	32.1	33.6	39.0	17.1	15.5
225	80.3	80.8	47.8	42.8	44.1	46.3	27.6	27.0
230	81.7	82.0	54.0	49.7	51.6	51.4	35.3	34.8
235	82.4	82.6	56.0	56.8	56.7	55.4	40.3	41.4
240			57.3	59.9	61.2	57.6	45.6	45.7
250			61.0	67.2	68.1	61.1	51.1	51.1
260			63.3	70.5	71.0	64.8	55.9	56.4
270			64.2	73.8	74.5	67.6	60.7	59.7
280			66.1	75.9	77.4	69.2	63.5	63.1
290			68.4	78.1	79.2	71.1	66.9	67.1
300			70.8	81.9	81.4	74.4	71.4	71.0
310			74.9	83.2	83.9	77.1	75.2	74.9
320			79.0	85.7	85.8	80.9	78.1	77.8
330			81.7			83.5	81.0	80.7
340			84.1				83.4	83.3
350							86.0	85.5
360							88.6	88.4
Pitch (Diffce)	7.7	7.75	7.6	7.8	7.7	7.95	5.7	5.9

TABLE XXXIII

Percentage by weight of products from distillation of crude phenols.

Source of crude phenols	Products from distillations, % by wt.							
	Water	Below 210°	210/ 240	240/ 270	270/ 310	Above 310°	Pitch	Loss
C.O. creosote oil	9.24	68.06	13.62				8.43	0.62
Tradeston heavy oil	7.70	24.89	30.37	6.70	11.27	9.91	8.17	0.99
B.F. creosote oil	6.20	6.62	52.55	13.41	9.72	2.31	8.38	0.81
MacLaurin L.T.tar	8.02	22.01	34.18	9.78	9.78	6.88	8.41	0.94
Shale oil	5.47	1.08	43.43	14.21	14.88	13.83	6.68	0.42

TABLE XXXIV

Yield of refined phenols etc. expressed as a percentage of the oil

Source of crude phenols	Crude phenols		Products from crude phenol distns.							
			% by wt.cr.phenols				% by wt. of oil			
	Wt. in grams	%by Wt. of oil	Wat-er	Phen-ols.	Pitch	Loss	Wat-er.	Phen-ols	Pitch	Loss
C.O.creos.oil	1136.5	18.94	9.24	81.71	8.43	0.62	1.75	15.48	1.60	0.11
Tradeston H.O.	561	9.35	7.70	83.14	8.17	0.99	0.72	7.78	0.76	0.09
B.F.creos.oil	1464	29.28	6.20	84.61	8.38	0.81	1.81	24.79	2.45	0.23
MacL.L.T.oil	758	32.80	8.02	82.63	8.41	0.94	2.63	27.11	2.76	0.30
Shale oil	1284	51.36	5.47	87.43	6.68	0.42	2.81	44.90	3.43	0.22

Physical Tests of the Refined Phenol Fractions

The specific gravity of the phenol fractions at 15.5°C was determined by the Westphal balance, with the exception of the fractions above 310°C which were too viscous. The Specific gravity of these higher fractions was determined by the pyonometer method.

The hydrocarbons in the phenol fractions were estimated by the following method, which is based on the procedure adopted by manufacturers of cresylic acids:-

20 gms. of the phenols were weighed in a beaker and heated over a water bath for 15 minutes with 80 c.c. of 9%-NaOH. The mixture was transferred to a separating cylinder and the beaker rinsed with 20 c.c. 9%-NaOH followed by 50 c.c. petroleum ether B.P. 60/80°C. The rinsing solvents were added in turn to the contents of the separating cylinder. The phenate and petroleum ether were mixed and settled, the phenate was drawn off and treated on two further occasions with 25 c.c. petroleum ether. The total ether extract was mixed, dried over anhydrous sodium sulphate, and the ether distilled off by adding the extract slowly to a weighed distilling flask which was immersed in a boiling water bath. The flask containing the residue from the ether distillation was placed in a steam oven for 15 minutes, then was blown out gently with air, cooled, and weighed. The flask was reheated in the steam oven and the constant weight of residue represented the hydrocarbons.

The results of the specific gravity and hydrocarbon determinations are shown in table XXXV, also the yield of the phenol fractions expressed as a percentage of the crude oils.

TABLE XXXV

B.P. phenol fractions	Blast-furnace creosote oil			MacLaurin L.T. tar oil			Shale-oil phenols		
	% Wt.	Sp.Gr.	%H.C.	%Wt.	Sp.Gr.	%H.C.	%Wt.	Sp.Gr.	%H.C.
Below 210°C	1.94	1.033	1.45	7.23	1.0405	0.60	0.56		
210/240 "	15.40	1.027	2.0	11.20	1.034	1.0	22.30	1.025	2.2
240/270 "	3.93	1.0298	4.35	3.21	1.048	1.25	7.30	1.023	3.0
270/310 "	2.85	1.073	6.85	3.21	1.095	1.85	7.64	1.0495	4.9
Above 310 "	0.67	1.097	11.70	2.26	1.126	5.45	7.10	1.079	7.2
	Coke-oven creosote oil			Tradeston heavy oil					
Below 210°C	12.9	1.0476	0.25	2.33	1.0447	0.40			
210/240 "	2.58	1.037	1.25	2.84	1.040	0.75			
240/270 "				0.63	1.0575	1.20			
270/310 "				1.05	1.1310	1.25			
Above 310 "				0.93	1.165	3.20			

The specific gravity of all the fractions is observed to decrease from 210°C and to increase above 240°C, with the exception of the shale-oil phenols which have a minimum density in the 240/270°C fraction. The phenols from high temperature tars have a higher specific gravity than the corresponding phenols from low temperature tars.

The hydrocarbons in every case increase with increase in the boiling point of the phenols. The hydrocarbons are abnormally high in all fractions of the blast-furnace phenols and the reason for this was traced to the washing of the oil. This oil was the first to be washed, and the small

quantity of emulsion which separated during the wash with 18%-NaOH was regarded as a very thick phenate and mixed with the rest of the true sodium phenate. The subsequent extraction of the phenate with benzol therefore has not entirely removed the entrained hydrocarbons. The increase in the percentage of hydrocarbons with rise in boiling point of the fractions is attributable to cracking although, in special cases, allowance may require to be made for the presence of partially phenolic bodies which are only soluble in sodium phenate and are extracted by the solvent. A special case of this nature occurs when methylated ether is employed instead of petroleum ether for the extraction of the phenate, as the following experiment shows:-

20 gms. of the shale-oil phenol fraction B.P. 310/358°C were dissolved in 100 c.c. 9%-NaOH and extracted with four successive 50 c.c. quantities of methylated ether during one test, and with the same quantity of petroleum ether B.P. 40/60° in the other test. The extracts were dried over anhydrous sodium sulphate and the ether distilled off until the temperature at the side tube was 150°C. The results were as follows:-

	Methylated ether extraction.	Petroleum ether extraction.
% Residue by weight	(1) 23.8	7.34
	(2) 23.0	7.50

The 23% residue smelled of phenols but formed an emulsion mainly and not a true solution with 18%-NaOH. The difference

in result with the solvents is probably due to the solubility of the phenolic asphalts, or rhetinols, in methylated ether and their insolubility in petroleum ether. The phenolic asphalts, which presumably are the low temperature tar phenols referred to by Morgan & Meighan (J.I.E.C., 1925, 17, 696), are said by these authors to be feebly acidic and largely hydrolysed in solution; this would account for their extraction from the phenate by methylated ether.

Emulsification of the Phenols and determination of the Disinfectant Values

It was decided that the black-fluid type of disinfectant emulsion would be the most satisfactory for the purpose of comparing the disinfectant value of the phenols, as the quantity of phenols available in the higher fractions was insufficient for the preparation of glue emulsions, except by laboratory methods, which did not give permanently stable products. A further reason which influenced the decision was that the ease of formation and stability of the glue emulsions decreased when high boiling phenol fractions were used. The black-fluid emulsions, in contrast, were more highly dispersed and difference in the phenol fractions did not influence either the ease of preparation, or the permanent stability of the fluid. The high boiling phenols, however, greatly retarded the rate of

dispersion of the fluids in water, but provided sufficient time was allowed for the soap to be adsorbed round the oil globules, and violent agitation during this period was avoided, then emulsions were formed which compared both in particle size determinations and in stability with previous emulsions of this type.

The concentrated fluids were prepared by the following formula:-

Phenols	= 35% by weight
Coke-oven neutral oil	= 45% " "
Sodium castor-oil soap	= 20% " "
(Castor oil = 57% on weight of soap)	

The soap, phenols, and neutral oil were weighed into a flask. The flask was fitted to a reflux water condenser and heated in a boiling water bath for 15 minutes in order to complete the formation of the fluid. The flask was cooled, re-weighed, and any loss, which never exceeded 0.1 gms., was made up with water. The density of the fluid was determined by the pycnometer method, and the percentage of phenols in the fluid was calculated on a volume basis.

The disinfectant value of the phenols was determined by the Rideal-Walker method, the broth was adjusted to pH 7.6 by the revised method (p.[illegible]). Greater care had to be observed in the preparation of the dilutions, in order to obtain proper dispersion of fluids containing the highest boiling phenol fractions. These fluids dispersed only slowly in water and it was found necessary to allow this

dispersion to proceed naturally, without violent agitation. If violently agitated before dispersion was complete, the soap in the fluid mixture was not adsorbed by the oil globules and an imperfect emulsion was obtained, which rapidly settled and contained visible oil globules. In a test with a 10% emulsion prepared from a fluid containing shale-oil phenols boiling above 310°, immediate agitation on a shaking machine, and similar agitation after slow dispersion of the fluid, gave these results:-

TABLE XXXVI

Method of preparing emulsion from fluid	Comparative settling tests of 10% emulsions			
	Time of settling - hours			
	1	5	24	72
By immediate agitation	15%	13%	11%	10%
By slow dispersion followed by agitation	½%	1%	2%	3%

The results prove that immediate agitation is detrimental to these fluids. Agitation after dispersion was complete was found to have no serious effect, and the dilutions were prepared by the method given on page 59 with the following slight modification. The dispersion of the fluid in the preliminary 2½% emulsion was obtained by intermittent gentle rotation of the bottle until the fluid was completely emulsified. After dispersion, which was complete within

5 minutes, the bottle was agitated on a mechanical shaker for 5 minutes. The preparation of the remaining dilutions from this emulsion and the technique of the test were exactly as described previously.

The results of the tests with fluids prepared from four of the oils are reported in table XXXVII; the number of tests made, the maximum and minimum coefficients, and the average coefficients are reported. Tests were not made with the coke-oven phenols, since the other results showed that no information of value would be gained.

The coefficients for the different fractions are obtained per unit volume of fluid which, on account of the differences in the density of the phenols, does not give a correct comparison. In table XXXVIII, therefore, results are calculated for the average R.W.Coefficient per unit volume and unit weight of (1) fluid (2) phenol plus hydrocarbon oil (3) phenol. Comparison of the results leads to the following conclusions:-

(1) The minimum and maximum coefficient values for comparative phenol fractions from the four oils are found to occur in the same oil, namely, the high temperature tar oil.

(2) A steady increase in the coefficient value with rise in boiling-point is obtained with the phenols from the high temperature tar oil, the maximum value being reached in the highest fraction boiling above 310°. In the case of all the low temperature tar phenols the maximum value is reached in the fractions B.P. 270/310°.

TABLE XXXVII

Rideal-Walker Phenol coefficients of fluids containing 35% by weight of the phenols reported below.

Source of phenols	B.P. of phenol fraction	No. of tests	Minm. coeff.	Maxm. coeff.	Average coeff.
Tradeston Heavy oil.	210/240°C	3	15	15.2	15.1
	240/270 "	3	25.4	27.3	26.2
	270/310 "	3	42	42	42
	310/-	6	60	66	62.5
Blast-furnace creosote oil	210/240 "	3	17	18	17.5
	240/270 "	3	32	34	33
	270/310 "	3	36	36.2	36.1
	310/-	6	28.5	30.4	29.3
MacLaurin low temp. tar oil.	210/240 "	4	16	17	16.4
	240/270 "	5	28.6	32.4	30.3
	270/310 "	3	38	40	38.7
	310/-	3	38	38	38
Shale oil	210/240 "	2	20	21	20.5
	240/270 "	3	29.5	30.5	30.
	270/310 "	5	32.4	34.3	32.7
	310/- "	3	24.8	26.6	25.7
Commercial H.B.tar acids	210/320 "	2	19	19	19

TABLE XXXVIII

Source of phenols	B.P. of phenol fraction	Dens. of phenols D_4^{15}	Dens. of fluid D_4^{15}	%by Vol. of C.O. N.oil	%by vol of phenols	R.W.coeff per unit of fluid.		R.W.coeff per unit of oil phase		R.W.coeff per unit of phenol	
						Vol.	Wt.	Vol.	Wt.	Vol.	Wt.
Tradeston heavy oil	210/240°C	1.038	1.0225	46.22	34.47	15.1	14.8	18.7	18.5	43.7	42.3
	240/270 "	1.055	1.0297	46.55	34.16	26.2	25.5	32.5	31.9	76.7	72.9
	270/310 "	1.129	1.0549	47.67	32.71	42.0	39.8	52.3	49.7	129	118
	310/-	1.1637	1.0638	48.08	31.99	62.5	58.8	78.1	73.5	195	168
Blast-furnace creosote oil	210/240 "	1.025	1.0179	46.0	34.75	17.5	17.2	21.6	21.5	50.4	49.1
	240/270 "	1.028	1.0198	46.07	34.70	33.0	32.4	40.9	40.5	95.0	92.5
	270/310 "	1.071	1.0338	46.73	33.79	36.1	34.9	44.8	43.6	107	99.7
	310/-	1.0953	1.0426	47.60	33.32	29.3	28.1	36.2	35.1	88	80.3
MacLaurin low temp. tar oil.	210/240 "	1.032	1.0215	46.17	34.65	16.4	16.1	20.3	20.1	47.3	46.0
	240/270 "	1.046	1.0272	46.43	34.37	30.3	29.5	37.5	36.9	88.1	84.2
	270/310 "	1.092	1.0415	47.2	33.38	38.7	37.2	48.0	46.5	116	106
	310/-	1.1235	1.0523	47.56	32.8	38.	36.1	47.3	45.1	116	103
Shale oil	210/240 "	1.023	1.0173	46.0	34.93	20.5	20.2	25.4	25.3	58.7	57.6
	240/270 "	1.021	1.0169	45.96	34.77	30.0	29.5	37.2	36.9	86.3	84.4
	270/310 "	1.047	1.0268	46.43	34.30	32.7	31.3	40.5	39.1	95.3	89.4
	310/-	1.076	1.0347	46.7	33.8	25.7	24.8	31.9	31.0	76.0	70.9
Commercial H.B.tar acids	210/320 "	1.028	1.0193	46.0	34.7	19.0	18.5	23.5	23.1	54.8	52.8

(3) Comparison of the density and coefficient value of the phenols B.P. 210/240° from the four oils shows that when the densities of the fractions are arranged in ascending order, the corresponding phenol coefficients of the fluids form a descending, or decreasing, parallel.

(4) No similar parallel is found in the comparison of the phenol fractions B.P. 240/270 unless the shale-oil phenols are excluded.

(5) Comparison of the density and coefficient value of similar fractions boiling above 270°C shows that in all instances the fraction having the greater density has the higher coefficient value. This result is the reverse of that observed in the lower fractions.

The theoretical reasoning connected with the explanation of these conclusions is deferred until after the submission of results for fluids prepared with pure phenols. It is of practical interest, however, to know which of the phenol distillates gives the higher average coefficient value and table XXXIX was prepared for this purpose. The average coefficients were calculated from the R.W. phenol coefficients per unit weight of fluid and the percentage weight of phenol distillate in each fraction. The fractions up to 210° are not included, since it is the usual practice when working for high boiling tar acids to cut the distillate at this point. The coefficient of the fraction up to 210°, when made up into a fluid, would not be greater than 8, and this value has been assumed in calculating the average phenol coefficient of the total distillate given in the final column.

TABLE XXXIX

R.W. phenol coefficients by weight of fluids prepared from phenols, as under:-

Source of phenols	Boiling-point range of phenols										Total distillate
	210/240	210/270	210/310	210/360	240/270	240/310	240/360	270/310	270/360	310/-	
Tradeston heavy oil	14.8	16.7	22.1	28.4	25.5	34.6	43.2	39.8	48.7	58.8	22.2
B.F.creos.	17.2	20.3	22.1	22.4	32.4	33.4	32.9	34.9	33.5	28.1	21.2
McL.L.T.Tar	16.1	19.1	22.4	23.9	29.5	33.4	34.0	37.2	36.8	36.1	19.0
Shale oil	20.2	22.5	24.3	24.4	29.5	30.4	28.6	31.3	28.2	24.8	24.2

The surprising feature of these results is the similarity in the coefficient values of the wide range fractions B.P. 210/310° and 240/310°. Large differences in the values occur only in the lowest and upper fractions. The low values in the 210/240° fractions occur where the proportion of phenols distilling below 210 represents about one-third of the total distillate, but higher results might have been obtained for these fractions if the lower boiling phenols had been better separated by column fractionation. It is of interest to note that the coefficient values of the phenols above 310° are greater, in every case, than the average coefficient value of the 210/310° fraction.

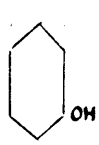
Colour of the Disinfectant Emulsions

The elimination of colour producing bodies from the phenols was not attempted, since this involved a complete research on the nature of the bodies producing the colour and the best means for their removal. The shale-oil phenols were most free from colour. Colour was not pronounced in the lowest boiling phenol fractions but increased in intensity with the higher fractions from 240°. The MacLaurin phenols were very bad and gave, in all except the 210/240° fraction, salmon pink to crimson coloured emulsions.

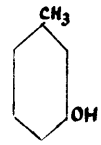
The cause of the colour of low temperature tar phenols was investigated recently by Burke & Caplan (J.I.E.C., 1927, 34, 19), who obtained a separation of the colour bodies using a saturated solution of borax, and successfully isolated one product, B.P.253°, which they determined to be a dimethyl pyrocatechol. The other unidentified products are designated as ortho-dihydroxy derivatives of high molecular weight hydrocarbons, probably derivatives of naphthalene or anthracene. Morgan (J.S.C.I., 1928, 47, 131T) gives a simple method for obtaining colour free true phenols from low temperature tar oils by washing the oils with 10%-NaOH saturated with brine. This method would probably have been adopted had it been known in time.

Disinfectant Values of Fluids containing Pure Phenols

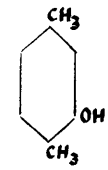
The preparation of fluids with pure phenols was found necessary in order to determine the relationship between the coefficient value of the fluid and the coefficient value of the phenol. The following homologous series of phenols was chosen:-



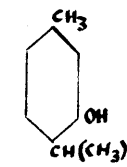
Phenol



m/Cresol



p/Xylenol



Thymol

The purity of the substances, as ascertained by the M.P., compared favourably with perfectly pure products, as follows:-

Phenol M.P. 40.6°	41°	(Washburn, "International Critical Tables" Vol. I)
m/cresol B.P. 202/203°	202.8°	do.
Thymol M.P. 51.2°	51.5°	do.
p/Xylenol M.P. 74.5°	74.5°	(Richter, 3rd Edn., Vol. I, 306)

In addition α/naphthol M.P. 95.5°(96°) and β/naphthol M.P. 121°(122) were used in the preparation of fluids. Fluids containing 35% by weight of the phenol were readily prepared with all except the naphthols, which crystallised out from the fluid. α/naphthol was more soluble than β/naphthol, however, and a stable fluid containing 20% of α/naphthol was prepared. The naphthols were more soluble in presence of cresol but the soap had to be increased in

order to obtain stable emulsions. The following three fluids were prepared with the naphthols, the proportions of the substances being by weight.

	I	II	III
α/Naphthol	20	20	
β/Naphthol			20
m/Cresol		15	15
Coke-oven neutral oil	60	45	45
Sodium castor-oil soap	20	25	25
(Castor oil = 57% on weight of soap)	100	105	105

The results of testing the pure phenol fluids by the Rideal-Walker method are recorded in Tables XL and XLI.

TABLE XL

Rideal-Walker phenol coefficients of pure phenol fluids.

Pure phenol in fluid	% by Wt. of constituents of fluid.			Dens. of fluid D_4^{15}	No.of R.W. Tests	Minm. coeff.	Maxm. coeff.	Aver. coeff.
	Phenol	Oil	Soap					
Phenol	35	45	20	1.0334	4	4.5	4.8	4.7
m/Cresol	35	45	20	1.0219	4	8.0	8.5	8.1
p/Xylenol	35	45	20	1.0233	3	11.0	12.0	11.7
Thymol	35	45	20	1.0247	4	32.4	34.0	33.2
α/Naphthol	20	60	20	1.0415	4	18	20	18.7
α/Naphthol 19 m/Cresol 14.3		42.9	23.8	1.0479	3	19	20	19.7
β/Naphthol 19 m/Cresol 14.3		42.9	23.8	1.0439	5	17	19	18.0

TABLE XLI

Pure phenol in fluid	Rideal-Walker phenol coefficients			
	per unit of fluid by vol.	per unit of fluid by wt.	per unit of oil phase by wt.	per unit of phenol by wt.
Phenol	4.7	4.5	5.6	12.9
m/Cresol	8.1	7.9	9.9	22.6
p/Xylenol	11.7	11.4	14.3	32.6
Thymol	33.2	32.3	40.4	92.2
α/Naphthol	18.7	17.9	22.4	89.5
α/Naphthol } m/Cresol }	19.7	18.8	25.8	56.5
β/Naphthol } m/Cresol }	18.0	17.2	23.6	51.6

These results for the pure phenols confirm the theory that the disinfectant value in a homologous series increases with increase in the number or length of the alkyl substituents. The large increase with thymol, which contains an isopropyl group in place of the methyl group in p/xylenol, is particularly noteworthy. α/napthol shows a lower coefficient value per unit of phenol than thymol and must have a lower disinfecting value, as previous results with these soap fluids have shown that the effect of increasing the percentage of phenols was to decrease this ratio. The coefficient of the α/naphthol and m/cresol fluid is slightly less than the proportional additive coefficients of fluids containing these phenols alone. By calculation the coefficient of the fluid by weight should be 20.2 and the coefficient per unit of phenol 60.8, but this difference

is within the experimental error of the Rideal-Walker test. Comparison of the fluids prepared with α/ and β/naphthols and containing the same proportion of m/cresol indicates that α/naphthol is superior to β/naphthol in disinfecting action.

The high coefficient of 4.5 for a fluid containing only 35% of phenol is sufficient evidence to prove that the disinfecting action is due to the combination of the phenol and hydrocarbon oil and not to the phenol alone. The hydrocarbon oil cannot be an inert diluent which simply assists in the emulsification of the phenols but must take an active part in the disinfection as, at the dilutions in which this fluid was tested, the phenol would be completely soluble in water. The increased disinfecting action might possibly arise from neutralisation of the positively charged bacteria by negatively charged emulsion particles, but another cause is the increased solubility of the hydrocarbon oil when in combination with phenol. Fränkel (p. 551) DRP (181, 288) says that aromatic hydrocarbons can be made soluble in water if one mixes with them water soluble aromatic hydroxyl derivatives, and cites as examples the addition of resorcin to cresol and of phenol to alizarin in order to obtain water soluble products. If the increased action is due to solution of the hydrocarbon oil then different oils will give different results and, by

experiment, blast-furnace oil was found very inferior to coke-oven oil. The literature on the toxicity of the hydrocarbon oils is limited chiefly to their action against wood destroying fungi and for this purpose the petroleum hydrocarbons are valueless while the coal-tar hydrocarbons are exceptionally effective. Bateman and Henningsen (Proc. Amer. Wood Pres. Assoc., 1923, 19, 136; Amer. C. Abs., 18, 2064) place the toxicity of benzene and naphthalene as 4 to 5 times as great as the corresponding phenols, and later report (Amer. C. Abs., 1925, 19, 3578) that the essential toxic principles of coal-tar creosote oil are the hydrocarbons boiling below 270°C. They consider that the high boiling tar acids and bases are the essential toxic materials of high boiling distillates such as carbolineum, the potentially toxic hydrocarbons being too insoluble to be effective. The hydrocarbons in the disinfectant fluids, it may be concluded, are definitely toxic, and will have a maximum disinfecting power when combined with the most soluble phenols. The comparison of the disinfectant value of the fluids, therefore, will not give a perfectly true comparison of the disinfecting value of the phenols, as, owing to the differences in the solubility of the phenols, the amount of hydrocarbon oil in solution will not be constant. The solubility of the phenols decreases with increase in the molecular weight, and the increase in germicidal value of the higher members

in combination with hydrocarbon oil will not be as great as results for the lower members of the pure phenol series would suggest.

Disinfectant Values of Pure Phenols and relationship of Chemical Structure to Germicidal Power.

The literature on the disinfecting value of pure phenols, although extensive, cannot be briefly summarised by interposition of a table of phenol coefficients, as the method of test and the organism employed are seldom the same. Tests by Cooper (B.M.J., 1912) on aqueous solutions of the cresols, employing B.typhosus as the test organism, gave a phenol coefficient value of 2.6 for all three isomers. The xylenols have been reported by many investigators to be superior to cresol and a coefficient value of 5 is given by Ishiwara (Z. Immunitats., 1924, 40, 429). The phenol coefficient value of thymol in aqueous solution has been reported to be 25 (Cooper, B.M.J., 1912,(1), 1234), 25 (Penfold and Grant, J.Proc. Roy. Soc. N.S.W., 1923, 38, 190) and 24 (Kingzett and Woodcock, Analyst, 1913, 38, 190). No satisfactory phenol coefficient value for the naphthols has been observed, but S. and E. K. Rideal ("Chem. Disinf. and Ster." p. 254) report that "α/naphthol is stated to be three times as powerful an antiseptic as the β/derivative". It will be noted that, although the order of increase of the fluids containing cresol, xylenol, and

thymol is the same, the phenol coefficient values are much greater than those reported for the pure phenols, and the relative increase in the coefficient value per unit of phenol from one member of the series to the next is less than is found for the pure phenols. These differences, as previously mentioned, are the result of the combination of the phenols with the hydrocarbon oil.

Several investigators have studied the comparison of the disinfecting value and the chemical constitution of the phenols, and the following results are of special interest. Laubenheimer ("Phenol und seine Derivate als Desinfektionsmittel" Berlin-Wien, 1909) found o/ and m/xylenol to be the strongest disinfectants of the higher phenols tested; his results were obtained by the garnet method and the summary of results is given in table XLII. Rapp (Desinfektion, 1909, 2, 617) observed that the disinfecting action of the following phenols decreased in the order:- pseuducumenol, xylenol, cresol, phenol.

Johnstone and Lane (J.A.C.S., 1921, 43, 348) prepared several of the alkyl derivatives of resorcinol, and observed an increase in the phenol coefficient value as the length of the side-chain increased. V. Leonard (J. Amer. Med. Assoc., 1924, 83, 2007) reports further results, as follows, for the alkyl resorcinols:- resorcinol, 0.3; ethyl-resorcinol, 1.5; n/propyl-resorcinol, 5.0; n/butyl-

resorcinol, 22.1; isobutyl-R., 15.2; n/amyl-R., 33.0; isoamyl-R., 23.8; n/hexyl-R., 46.0; n/heptyl-R., 30.0. The very high phenol coefficient values and the attainment of a maximum value in n/hexyl-resorcinol are of special interest. Tilley and Schaffer (J. Bact., 1926, 12, 303) report results for alkyl derivatives of the monophenols by the Rideal-Walker method, viz., p/cresol, 2.5; p/ethyl-phenol, 7.4; p/propyl-phenol, 21.6; p/butyl-phenol, 68.0. The boiling-points of these four phenols were respectively 202°, 217°, 232°, and 248°. S. and E. K. Rideal (book, p. 254) mention that the tetrahydronaphthols are said to be more powerful germicides than the naphthols, also (p. 237) that trimethyl-methoxy-phenol is stated to have a Rideal-Walker phenol coefficient value of 40, when properly emulsified.

The analysis of these results shows that exceptionally high coefficient values are obtainable with phenols containing either a long aliphatic side-chain, or a number of alkyl substituents.

TABLE XLII

(K. Laubenheimer, "Phenol u. seine Derivate als Desinfektionsmittel", Habilitationsschrift, Giessen, 1909, p.145)

Time after which staphylococci were killed	Disinfecting agent in 1% solution	Hydrotropic or emulsifying agent.
30 seconds	o/Xylenol	Pot. dioxystearate
"	m/Xylenol, asym.	" "
"	"	" sulphoricinoleate
"	"	" ricinoleate
1 minute	m/Xylenol, sym.	" "
2 minutes	Thymol	" dioxystearate
	Isopropyl-p-cresol	" "
3 minutes	Thymol	Sod. Sulphoricinoleate
"	Propyl-phenol	Pot. "
"	m/Xylenol, asym.	" soft soap
4 minutes	Propyl-m-cresol	" sulphoricinoleate
"	Propyl-p-cresol	" "
"	" "	" dioxystearate
"	Isopropyl-p-cresol	" sulphoricinoleate
6 minutes	Isopropyl-m-cresol	" "
"	Isobutyl-p-cresol	" "
7 "	Crude propyl-cresol	" dioxystearate
"	Propyl-o-cresol	" sulphoricinoleate
8 minutes	Isopropyl-o-cresol	" "
9 minutes	p/Xylenol	" ricinoleate
12 minutes	Isopropyl-phenol	" sulphoricinoleate
15 minutes	β/Naphthol	" dioxystearate
	Isobutyl-phenol	" sulphoricinoleate
18 minutes	Crude isopropyl-cresol	" dioxystearate
	Amyl-phenol	" sulphoricinoleate
20 minutes	Amyl-m-cresol	" "
	amyl-p-cresol	" "
25 minutes	Isobutyl-o-cresol	" "
30 "	" -m- "	" "
	Amyl-o-cresol	" "
90 "	Phenol	water

Disinfectant Value of Impure Phenol Fractions and Relationship to Pure Phenols

The only results observed which provide data on the disinfectant value and boiling-point range of commercial phenols are those of Cooper (B.M.J., 1912). He dissolved the phenols in potash castor-oil soap and obtained a concentrated fluid which formed a milky emulsion in water. The results of tests, using B. typhosus as the test organism, are reported in table XLIII.

TABLE XLIII

(E. A. Cooper, B.M.J., 1912,(1), 1234, 1293, 1359)

B.P. of phenol fraction	%ge phenols in fluid	Phenol coeff. of fluid	Phenol coeff. per unit of phenol.
205/209°	62.5	6.8	10.9
209/218	"	7.2	11.5
218/225.5	"	9.5	15.2
225.5/240	"	14.1	22.5
240/274	50	13.8	27.6
274/286	"	13.0	26.0

The phenol coefficient of the fluid containing 50% of phenols B.P. 240/274° is much less than the phenol coefficients of the author's fluids, which contained 35% of similar phenols with hydrocarbon oil in addition. The phenol coefficient per unit of phenol in this fluid is also less than was obtained for glue emulsions containing 50% of commercial high boiling tar acids, which were lower in

disinfecting value than the 240/270° fractions from any of the four oils.

Comparison of the phenol coefficient values of disinfectant fluids prepared with pure phenols and of fluids prepared with the phenol fractions from several oils shows that the lowest 210/240° phenol fractions contain products of greater germicidal power than p/xylenol. The fractions B.P. 240/270° contain substances of equal disinfecting value to thymol in combination with substances of lower value. The next fractions B.P. 270/310° apparently contain derivatives of naphthol of greater germicidal power than naphthol alone. The final fractions probably contain derivatives of anthranol and phenanthrol, the disinfectant values of which are unknown.

The reduction in the phenol coefficient values of the final fractions of the low temperature tar phenols cannot be attributed to cracking since the percentage of hydrocarbons, although increased, is insufficient to account for the very great reduction observed in the shale-oil phenols. The more probable reason for this reduction is the presence of complex phenols, which are not sufficiently soluble in water to exert a toxic action. A similar maximum germicidal power is reached with n/hexyl-resorcinol in the homologous series of alkyl resorcinols (already reported) and Morgan (J.S.C.I., 1926, 448T) reports that the low temperature tar phenols distilling at 350° have a

maximum phenol coefficient of 27 in a 50% emulsion with soap. Before discussing reasons for the differences in the disinfecting action of the phenols in comparative fractions from the four oils, a summary of the phenols which have been isolated from tars and the indications which physical tests show will be of benefit.

Phenols identified in Commercial Tars

High Temperature Tars.

Phenol and the three cresols are the main constituents. In addition to these, the three xylenols ($CH_3:CH_3:OH$), 1:3:5 (B.P.218°), 1:2:3 (213°), and 1:2:4 (225°), have been isolated by Schulze (Ber., 1887, 40, 410), who also was successful in separating the two isomeric naphthols (Ann., 1885, 227, 143). Nölting (Ber., 1884, 17, 386) obtained evidence of the presence of hydroxyl derivatives of anthracene and phenanthrene in the fraction of anthracene oil boiling above 300°.

Blast-Furnace Tar.

Watson Smith and co-workers (J.C.S., 1886, 49, 17T; J.S.C.I., 1883, 495; 1887, 583) found only low percentages of phenol and cresol in this tar, and indications of xylenols, pseudocumenols and naphthols. 1:3:4 xylenol is reported by Lunge ("Coal Tar and Ammonia" 5th Edn. 1916, 278) to have been found by W. Smith in this tar. Edwards (J.S.C.I.,

1924, 43, 143T) observed that the phenols from this tar were very closely related to phenols from other true low temperature tars and his results will be given when discussing these tars.

Shale Oil.

T. Gray (J.S.C.I., 1902, 21, 845) examined the phenols from the green naphtha fraction of shale oil. The crude phenols represented approximately 0.05% of the oil and consisted of from 5/6% phenol, 12/15% o/cresol, 30/35% m/cresol, 30/35% xylenols 1:2:4 and 1:3:5, and 16% phenols boiling above 230°C. P. N. Kogerman (J.S.C.I., 1927, 46, 137T) examined the 230/270°C fraction of an Estonian shale oil, which was exceptionally high in phenols, viz., 22.4%. This fraction represented 8% of the crude Kukersite oil and contained 17.2% of phenols, from which o/, m/, and p/cresols, principally m/cresol, and 1:4:5, 1:2:4 and 1:3:4 xylenols were isolated and identified. The presence of mesitol or propylphenol was indicated. Phenol ethers of the guaiacol type were present but not isolated. The phenols resinified within a few minutes on contact with saturated sodium hydroxide and the cause of this condensation (or polymerisation) is ascribed to the presence of phenols with unsaturated side-chains (or aldehydic groups in the side-chains). There is nothing known at present regarding the nature of the higher phenols in shale

oil except that they resemble low temperature tar phenols.

Low Temperature Tar.

Much work has been done in recent years on the low temperature tar phenols which is summarised by E. Parrish (History of L.T. Tar, Fuel 1926, 5, 436/465). The phenols identified have been phenol, in traces, o/, m/ and p/ cresol; 1:3:5, 1:2:4, 1:4:2, 1:3:4 and 1:4:5 xylenol, indications of trimethyl phenols have been found, also of phenols with unsaturated side-chains in the range of the tetramethyl phenols. β/naphthol has been isolated by Weindal (Brennstoff Chem., 1922, 3, 248) and α/ and β/naphthol have been identified by several but not all investigators. The presence of naphthol derivatives has been indicated and are estimated by Morgan and Soule (Chem. and Met. Eng., 1922, 26, 923, 977) to represent 10% of the total phenols. The phenols from low temperature tar have been separated into two portions by the use of petroleum ether. The petroleum ether soluble phenols are considered to be true homologues of phenol and the insoluble residues have been referred to as phenolic asphalts. The specific gravity of these phenolic asphalts ("rhetinols" Edwards) is given by Edwards (J.S.C.I., 1924, 43, 143T) as 1.115 and by Parrish & Rowe (J.S.C.I., 1926, 45, 99T) as 1.133. Weindal (Brennstoff. Chem., 1923, 4, 321) and Edwards observe that they give true phenols on

distillation. The distillation at atmospheric pressure is stated by Edwards to commence at 300°C with decomposition into water, light aromatic hydrocarbons, true phenols, and pitchy residues, with at least 40% of the rhetinols passing over unchanged with the phenols. The proportions of the petrol soluble and insoluble phenols, according to Edwards, are respectively 51.8% and 45.1% in blast-furnace tar phenols, and 46.8% and 50.5% in MacLaurin L.T. tar phenols. The specific gravities and boiling-points of the true phenols are much lower than those of the rhetinols, or the combined distillates of true phenols and rhetinols, and Edwards advances the hypothesis that the phenoloid distillates consist of a mixture of the homologues of phenol boiling up to 240/260°, and of steadily decreasing specific gravity, in combination with high boiling rhetinols. In support of this hypothesis he finds that the temperature rises rapidly at 260°, during the distillation of the true phenols, and the residue in the flask is insoluble in petroleum ether and identical with the rhetinols. The rhetinols are said to be superior to tricresol in disinfectant value.

Edwards and Morgan and Soule, by plotting the specific gravity of the phenols against the boiling-point, show that a minimum specific gravity is attained, at 235° according to Edwards, which is followed by a rapid rise, with increasing viscosity of the phenols. The initial fall is

attributed to methylated homologues of phenol with an increasing length of aliphatic side-chain attached to the phenol nucleus, and the final rise and increase in viscosity to polynuclear phenols.

Other investigators have determined the average molecular weight of the phenol fractions in order to elucidate their chemical structure. Weindal (Brennstoff. Chem., 1922, 3, 245) obtains an increase in the molecular weight from 200° to 240°, where a maximum is reached, then a slow decrease to 270/280° and finally a rapid rise. Suggestions of either unsaturated polyhydric phenols, or phenols of the oxybenzyl-alcohol type, are submitted in explanation of the decrease from 240°. An o/dimethyl-pyrocatechol B.P. 253°, S.G.(25°) 1.1426, M.W. 139, has been isolated from low temperature tar by Burke & Caplan (J.I.E.C., 1927, 34, 19), also higher homologues which are designated ortho dihydroxy derivatives of hydrocarbons of high molecular weight, probably homologues of naphthalene or anthracene.

G. T. Morgan (J.S.C.I., 1928, 47, 132T) reports that the results obtained at the chemical research laboratories, Teddington, so far suggest that the aromatics of low temperature tar are often the methyl derivatives of those from high temperature tar.

It would appear from the above summary that the phenols of low temperature tar resemble the phenols in high

temperature tar, but the lower boiling fractions have longer, or more numerous, aliphatic side-chains attached to the phenol nucleus and the higher boiling fractions contain polynuclear phenols, possibly hydrogenated and/or methylated derivatives of those present in high temperature tar.

Discussion on the results of the Germicidal Tests of the Phenols from various Oils

The comparison between the low and the high temperature tar phenols shows several distinctive features. One of the main distinctions is that the disinfectant values of the lower fractions of low temperature tar phenols are greater than those of the corresponding fractions from high temperature tar phenols. This increase in disinfectant value is in conformity with the generally accepted view that low temperature tar phenols have longer, or more numerous, aliphatic side-chains attached to the phenol nucleus. Phenols, however, with longer, or more numerous, aliphatic side-chains have lower specific gravities, therefore, according to theoretical reasoning, phenol fractions with lower specific gravities should have higher disinfectant values. This relationship is found true in the 210/240° phenol fractions, and the phenols are found in the same

order when arranged according to decreasing specific gravity, or increasing disinfectant value. A parallel relationship between specific gravity and disinfectant value is also found in the phenol fractions B.P. 240/270°, if the shale-oil phenols are excluded. It is permissible to conclude, therefore, on the basis of both disinfectant value and density determinations, that the low temperature coal-tar phenols boiling below 270° have longer, or more numerous, aliphatic side-chains attached to the phenol nucleus than the corresponding high temperature coal-tar phenols.

The shale-oil phenols are best considered separately, as they differ from the coal-tar phenols in two respects, viz., they are lower in specific gravity than the phenols from other sources while the increase in disinfectant value as the boiling-point rises is less marked. The lower specific gravity and higher disinfectant value of the 210/240° fraction, compared with the coal-tar phenols of the same boiling-point, indicate that the shale-oil phenols of this fraction have even longer, or more numerous, aliphatic side-chains attached to the phenol nucleus than the low temperature coal-tar phenols. The same statement, however, cannot be made for the shale-oil phenols B.P. 240/270° as, although the specific gravity of this fraction is lower than that of the corresponding low temperature

coal-tar phenols, the disinfectant value is not greater, but equal to the "Maclaurin" L.T. tar phenols and less than the blast-furnace tar phenols. The presence of dihydric phenols in quantity might explain the lower result, but the almost complete absence of red colour in the emulsion prepared with this fraction does not support this suggestion. The very low specific gravity of this fraction, also the comparatively low densities of the higher fractions, suggest that these phenols are more highly hydrogenated, or methylated, than the corresponding low or high temperature coal-tar phenols. Hydrogenation or methylation of phenols, however, gives products of lower solubility and with the higher phenols the reduction in solubility may be sufficient to reflect on the germicidal activity. It is this factor apparently which is operative in the case of the shale-oil phenols, and the solubility of the phenols in the fraction boiling above 310° appears to be so low, compared with the other fractions, that the disinfectant value is less than either the 270/310° or 240/270° fractions. The above presumption, therefore, that shale-oil phenols are more highly hydrogenated, or methylated, than coal-tar phenols would account for the lower specific gravities of these phenols and, at the same time, explain the less rapid rise in the disinfectant value of the phenols with rise in boiling-point. The

comparison of disinfectant value and specific gravity in the shale-oil phenol fractions boiling above 270° is in alignment with the phenols from other sources and will be treated further in conjunction with them. Time has not permitted any chemical examination of the shale-oil phenols to be made, but this study is being pursued by my successor to the "Ferguson Fellowship".

The results for the disinfectant values of the phenols boiling above 270° are of special interest, as beginning with the 270/310 fraction there is a complete change in the relation between specific gravity and disinfectant value, the phenols of greatest density now having the maximum disinfectant value. The polynuclear phenols which occur in this range in high temperature coal tars have higher densities than the hydrogenated and/or methylated derivatives previously referred to and assumed to be present in low temperature tars. Comparison of the disinfectant values together with the specific gravities of the higher phenol fractions shows that the presumably aromatic polynuclear phenols of the high temperature tar have greater disinfectant values than the corresponding hydrogenated and/or methylated derivatives of the low temperature tars. Further, the increase in disinfectant value with increase in specific gravity of the low temperature tar phenols boiling above 270° probably indicates the presence of increasing proportions of aromatic polynuclear phenols.

The phenol coefficient value per unit of tar acid of the 270/310° fraction from high temperature tar is shown to be considerably greater than the corresponding value for α/naphthol, and the disinfectant value of the following fraction boiling above 310° is still greater than the 270/310° fraction itself. Therefore the phenols of greatest germicidal power in high temperature tars would appear to be aromatic polynuclear phenols of the type of anthranol and phenanthrol, and the high phenol coefficient of the 270/310° fraction may be explained by the inclusion of part of these higher germicidal phenols with the naphthols.

In the low temperature tars the disinfectant values of the phenol fractions B.P. 270/310° are less, in every case, than the value of the corresponding fraction from high temperature tar. These phenol fractions, however, have phenol coefficient values per unit of tar acid equal to, or slightly greater than, the corresponding value for α/naphthol. This result might be explained by the presence of higher aromatic polynuclear phenols in less quantity than in the corresponding high temperature tar fraction. Another explanation which supports the view that the low temperature tar phenols are chiefly hydrogenated and/or methylated derivatives of the high temperature tar phenols can be advanced. Tetrahydronaphthol, for instance, is a simple hydrogenated naphthol derivative which is known

to have a greater germicidal value than naphthol itself, and it seems possible that it or similar hydrogenated and/or methylated naphthol derivatives in the 270/310° fractions of the low temperature tar phenols may be responsible for these fractions having disinfectant values greater than that of α/naphthol but less than the higher aromatic phenols. The maximum disinfectant value of the low temperature tar phenols is reached at the naphthol derivative stage as, judging from the results of the phenol fractions boiling above 310°, hydrogenation or methylation of still higher polynuclear phenols does not increase the disinfectant value, which may be accounted for, as already mentioned in the course of the discussion on the shale-oil phenols, by the insoluble nature of the products leading to a reduction in the germicidal value. The reduction in germicidal value is shown by all the low temperature tar phenol fractions boiling above 310° and the disinfectant values of these fractions are lower than the previous 270/310° fractions, averaging only about one-half of that of the corresponding high temperature tar fraction.

The conclusion arrived at, therefore, in the comparison of the phenol fractions boiling above 270° is that the high temperature tars contain phenols of the type of naphthol, anthranol, and phenanthrol, which are of high disinfectant value and, with the exception of naphthol, do

not appear to be present in low temperature tars, in quantity.

The comparison of the disinfectant value of the phenols from the four sources examined leads to the following conclusions regarding the temperatures under which the tars were formed. The truest low temperature phenols are those from shale oil, as they show the maximum disinfectant value at the lower boiling-points and the maximum reduction in disinfectant value at the higher boiling-points, which may be caused by the insolubility of the complex and highly substituted phenols. For the same reasons the other tars are placed in the following order indicating higher temperature and increased cracking during production, viz:-

Blast furnace tar.
"MacLaurin" low temperature tar.
"Tradeston" horizontal retort tar.

GENERAL CONCLUSIONS

The disinfectant values of the phenols from low and high temperature coal-tars and shale oil have been determined and are found to confirm accepted deductions regarding their chemical composition made from known physical and chemical data.

An important result of the present investigation is that the phenols of greatest germicidal power have been found in high temperature coal-tar.