

ALUMINIUM STEARATE GELS IN LIGHT HYDROCARBON OILS.*

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SYNOPSIS.

An account is given of the preparation and properties of "gels" of aluminium stearate in various solvents, including benzene, *cyclohexane*, *cyclohexene*, and petrol. The effects of so-called peptisers—phenols, alcohols, etc.—on the gelation process and gel properties are described.

The effect of variables, such as concentration of soap and peptisers, moisture content of soap and conditions of preparation on the stability of the products was examined. Other properties of the gels considered included the phenomenon of anomalous viscosity and temperature sensitivity.

INTRODUCTION.

THE Mixtures Committee, an Advisory Committee of the Petroleum Warfare Department from 1940 to 1946, was concerned with the devising, investigation, and development of incendiary mixtures for use in a wide variety of munitions of war. The committee was formed in the summer of 1940 under the chairmanship of the late Director of Fuel Research, Dr. F. S. Sinnatt. After his death in January 1943, Professor Sir Alfred Egerton was chairman until the committee was disbanded in March 1946.

Research and development work on different projects was carried out by various members of the committee, each of whom had the benefit of the advice and guidance of the committee as a whole. From 1940 to 1945, at least one team, and often two or more teams, worked continuously at the Fuel Research Station for the committee, and in addition carried out a considerable amount of work directly for the Petroleum Warfare Department.

Experimental investigations concerned with the devising and study of incendiary mixtures for various purposes were carried out at the Station and will be described in a paper entitled "Incendiary Fuels for Various Purposes."¹ The most important work was the study of the preparation and properties of fuels for flame-throwers, and in particular the creation and development of the aluminium stearate petrol gels known as FRAS flame-thrower fuels. An account of these fuels will be given in a paper entitled "Aluminium Stearate Gels for Use as Flame-Thrower Fuels"²; the present paper records the results of some of the studies of the gelation of aluminium stearate in hydrocarbon oils which were made during the course of the development of the fuels.

(Note.—There are different opinions as to the precise significance to be attached to the terms "gel," "sol," and "jelly." When aluminium stearate is dispersed in a hydrocarbon solvent to give a free-flowing colloidal solution, the product is perhaps more properly termed a "sol,"

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but the term "gel" has been used throughout the work and the process has always been described as "gelation.")

Literature.

The property of aluminium stearate of forming sols or gels in hydrocarbon oils is well known and has found technical application for a number of purposes, such as the manufacture of soaps and lubricating greases. The formation of jellies by aluminium soaps in organic solvents was studied in 1932 by McBain and McClatchie,³ and in 1935 Ostwald and Riedel⁴ showed that aluminium soaps in benzene solution exhibit structural viscosity, the effect increasing with increase in concentration. The latter workers also drew attention to the influence of moisture in the soap in reducing viscosity of the gel.

Much of the work with aluminium stearate and other aluminium soaps has been carried out with the commercial products. These have been made by double decomposition between aqueous solutions of the sodium soap and an aluminium salt, and are usually available as fine, white powders. They are not single chemical compounds but are mixtures, containing a proportion of "free" fatty acid⁵ which is readily extracted by means of organic solvents. The influence of this "free" acid in reducing the viscosity of gels in organic solvents has been recognized by users.⁶

According to Eigenberger⁷ a considerable difference exists between the compositions of aluminium stearates prepared by double decomposition in aqueous solution, and by the reaction of the free fatty acid with aluminium hydroxide. Previously he⁸ had been unable to prepare aluminium di- and tri-stearates. McBain and McClatchie⁹ have stated that the latter cannot be prepared even in completely non-aqueous media, but according to Lawrence (private communication) the preparation can be effected under suitable conditions. In any case, it is generally supposed that the usual commercial product consists of a mixture of the mono-stearate and di-stearate with a proportion of "free" stearic acid. According to Ostwald and Riedel,⁴ the composition of their aluminium soaps varied from 1.1 to 1.6 atoms Al per 3 mol fatty acid.

A wide study of the preparation and properties of metal soaps and their gelation in hydrocarbon and other solvents has been made by Lawrence.¹⁰ His work on the action of peptisers and especially the effect of such substances as cresol and amyl alcohol in increasing the solubility and lowering the gelation temperature of sodium stearate in hydrocarbon solvents,^{10 (v)} is of particular interest and importance in connexion with the present work.

Mention must also be made of the great volume of work on the preparation and properties of aluminium soaps which was carried out during the war in the United States, but is as yet unpublished. Close liaison between British and American workers in this field was maintained throughout the war.

Materials.

Aluminium Stearate.

An account of the developments by A. Boake, Roberts and Co. Ltd., of a suitable grade of aluminium stearate for the preparation of petrol gels

has been given elsewhere.² The material used in the experiments described in this paper was supplied by the Sandoz Chemical Company. It was a granular white powder having the following properties :

Bulk density	0.35-0.45 g/ml
Moisture content	1.0 per cent
" Free acid " content :	
(a) extraction with cold alcohol (100 ml with 2 g soap)	2.7 " "
(b) extraction with boiling acetone	2.2 " "
Soluble ash (mainly Na_2SO_4)	0.9 " "
Insoluble ash (mainly Al_2O_3)	9.8 " " *

* This corresponds to 1 atom aluminium to 1.5 mol acid.

The stearine used in the preparation of the aluminium stearate was a commercial grade containing about 50 per cent palmitic acid and 8 per cent oleic acid.

Petrol.

Petrol was used for the preparation of many of the gels. Except where otherwise stated, the petrol used was obtained from a single consignment obtained from the Pool Board. The petrol was stored in a sealed container in contact with only a limited amount of air and was not exposed to light except during the preparation of the gels. All the samples for which results are quoted in this paper were prepared during a period of only a few weeks, and it is therefore reasonable to assume that there was no significant change in the composition of the petrol during the experiments.

The petrol, which was undyed and was free from tetra-ethyl lead, had the following properties :

Density, d_4^{20}	0.7372
Boiling range :	
I.B.P.	47° C
At 50° C, vol per cent	3
At 100° C " " "	35.5
At 150° C " " "	77
At 180° C " " "	95
F.B.P.	191° C
Composition, wt per cent :	
Unsaturated hydrocarbons	29
Saturated hydrocarbons	62
Aromatic hydrocarbons	9
Peroxide value, active oxygen g/litre petrol	0.012

Xylenols.

Mixed xylenols, a commercial product, was used as a peptiser in the preparation of many of the mixtures. The material was supplied by P.R. Chemicals Ltd. who also provided the information given below. The sample consisted of the whole distillate to pitch from cresylic acid as washed from high-temperature coal-tar (a mixture of tars from horizontal and vertical retorts) after the removal of the greater part of the phenol and cresol, and with the addition of 2.5 per cent of high-boiling tar acids (distilling approximately 60 per cent at 270° C) of coal-tar origin.

The sample contained traces of phenol and about 4 per cent of cresols ;

the bulk of the material consisted of the xylenols, with a substantial proportion of the ethyl phenols and higher homologues.

Moisture content, per cent	0.48
Sp.gr. at 15.5° C	1.022
Density, d_4^{20}	1.0171
Distillation range :	
I.B.P.	215.4° C
45 per cent boils up to	220° C
82 " " " " "	225° C
95 " " " " "	230° C

Other Materials.

Many other substances were used as solvents and peptisers. It was not possible when the work was carried out to use specially purified materials, but every care was taken to obtain the purest materials commercially available. An indication of the purity is given by the following physical data :

Substance.	Melting Pt, ° C.	Density, d_4^{20} .
Benzene (crystallizable)	—	0.8757
cycloHexane	—	0.7787
cycloHexene, distilled and washed with sodium bisulphite to remove peroxides	—	0.8103
Light petroleum (b.p. 80–100° C—free from aromatic hydrocarbons)	—	0.7144
<i>o</i> -Cresol	28	—
<i>m</i> -Cresol	—	1.0350
<i>p</i> -Cresol	32	—
2 : 4-Xylenol	—	1.0208
3 : 4-Xylenol	65.5	—
2 : 5-Xylenol	73	—
3 : 5-Xylenol	63	—
Catechol	104.5	—
Resorcinol	110	—
Hydroquinone	170	—
Pyrogallol	122–127	—
Methyl alcohol	—	0.7909
Ethyl alcohol	—	0.7904
<i>n</i> -Propyl alcohol	—	0.8049
<i>n</i> -Butyl alcohol	—	0.8111
Ethyl cellosolve	—	0.9308
Oleic acid	—	0.8989
Acetone	—	0.7898
Pyridine	—	0.9831

Apparatus and Procedure.

The gelation of aluminium stearate in hydrocarbon solvents occurs at temperatures above ordinary atmospheric temperature, and the method of gelation used in this investigation was therefore to mix the components by means of a mechanically operated stirrer while supplying heat from an electric furnace. The apparatus is illustrated in Figs. 1 and 2.

In general the size of the sample prepared was 360 ml. The requisite amount of aluminium stearate powder was weighed into a 2-lb Kilner jar and covered as quickly as possible with 360 ml of the hydrocarbon solvent. The peptiser was then weighed out and washed into the jar with the amount

of the solvent (usually about 5 ml) required to compensate for loss by evaporation during heating. (When the solvent was a mixture of hydrocarbons of different volatility, such as petrol, the compensation was, of course, not exact.) The jar was clamped in position over an electric furnace, the mouth of the jar being filled by a cork fitted with a thermometer and a power-driven mild-steel stirrer. When in use the stirrer normally revolved at 600 ± 50 r.p.m. The position of the furnace was adjusted so that the temperature of the contents of the jar was raised at the rate of 1°C per minute.

The process of gelation is illustrated in Figs. 3, 4, and 5. At first, the action of the stirrer produces a vortex in the suspension (Fig. 3), but at a certain, fairly well-defined temperature, an increase in the viscosity of the liquid becomes apparent, and the vortex disappears leaving a level liquid surface (Fig. 4); the temperature at which this phenomenon occurred was recorded in these experiments as the "gelation temperature."

After gelation, heating was continued so as to raise the temperature by 10°C in 1 hour, the rate of heating being reduced in order to achieve a rise of 5°C in the first 20 minutes and a further 5°C in the subsequent 40 minutes. During this period the gel thickens and climbs the shaft of the stirrer until the surface of the gel is cone-shaped (Fig. 5).

The furnace was then lowered away from the jar, and stirring continued for a further 10 minutes while the gel cooled slightly. The jar was removed from the clamp and the contents transferred as completely as possible to a cylindrical glass bottle of 450 ml capacity, having an internal diameter of about 5 cm so that the depth of the gel was at least 13 cm. The bottle was sealed and the sample normally stored at laboratory temperature for a day before measurements of viscosity were made.

(Note :—The concentrations of soap and peptisers quoted in this paper as percentages were always measured on a weight/volume basis [*e.g.*, 5 per cent = 5 g/100 ml].)

Measurement of Viscosity.

The apparent viscosity of the gel was measured by observing the time required for a 5/32-inch diameter steel ball to fall 5 cm through the sample. The result was described as the "ball-drop viscosity" and was expressed in seconds.

The sample was contained in a glass tube or bottle having an internal diameter of at least 5 cm and the ball was allowed to fall centrally. The depth of the sample was such that the ball had to fall at least 5 cm in order to attain its terminal velocity before a measurement was made, and there was always at least 3 cm of gel below the lower mark of the measured 5 cm fall. The sample was maintained at the required temperature in a thermostatically controlled water bath for at least 3 hours before the viscosity was measured. The viscosity was taken as the average of three or four determinations provided the agreement was close; if the results varied by more than ± 1 per cent (which rarely happened) the sample was discarded.

In a study of the viscometry of soap-in-hydrocarbon systems, Wood, Nissan and Garner¹¹ made an examination of the factors affecting viscosity measurements by this method.

Gelation Without Peptisers.

A series of gels with different concentrations of aluminium stearate was made with several solvents. The gelation temperature was recorded, and observations of the appearance of the gels were made over a period of 3 months.

Petrol.

TABLE I.

Gelation in Petrol without Peptisers.

Concentration of al. stearate, g/100 ml petrol.	Gelation temperature, ° C.	Appearance of gel immediately after cooling.	Time after which syneresis was observed.
2	61	Weak, heterogeneous gel	2-3 days
4	60	Thick, stringy gel	36 hours
5	57	Very thick gel	26 hours
6	57	Very thick gel	20 hours
8	56	Thick, hard grease	18 hours

Increase in the soap concentration was accompanied by a small but definite lowering of the gelation temperature; the same effect was observed with all solvents. The gels were all white and opaque, and were so viscous at the higher concentrations that the soap was not uniformly dispersed.

The mixture containing 2 per cent of soap was a weak, free-flowing gel which gradually changed to a thin grease which showed syneresis after 2 to 3 days. Similar phenomena were observed with all the mixtures, the gels becoming more viscous and less stable with increase in soap concentration.

Light Petroleum.

The solvent used was a light petroleum of b.p. 80 to 100° C, free from aromatic hydrocarbons.

TABLE II.

Gelation in Light Petroleum without Peptisers.

Concentration of al. stearate, g/100 ml petroleum.	Gelation temperature, ° C.	Appearance of gel immediately after cooling.	Time after which syneresis was observed.
2	62	Weak gel	24 hours
4	60	Thick moderately stringy gel	18 hours
5	60	Very thick gel	5 hours
6	60	Very thick gel	5 hours
8	59	Thick grease	4 hours

The gels obtained were similar to those prepared in petrol, but syneresis occurred more rapidly. The mixtures containing 2 and 4 per cent of soap, at first showed slight sticky and stringy properties, but these soon

disappeared and syneresis occurred within 24 hours. By this time the gel of lowest concentration had changed to a very thin, free-flowing grease, and the remaining mixtures were white, opaque greases (increasing in hardness with increased soap concentration) and were somewhat less brittle than the corresponding mixtures in petrol. These greases showed marked thixotropy, and on vigorous shaking the separated liquid was re-absorbed to give uniform thin creams. While being shaken the mixtures were almost as mobile as water, but immediately shaking was stopped they reverted to non-flowing greases, from which solvent separated on standing.

cycloHexane.

The gels prepared in *cyclohexane* were moderately clear, cloudiness increasing with increased soap concentration. Compared with gels prepared in petrol and light petroleum, the gels in *cyclohexane* were relatively stable, and showed syneresis only after 3 to 4 weeks.

TABLE III.

Gelation in cycloHexane without Peptisers.

Concentration of al. stearate, g/100 ml <i>cyclohexane</i> .	Gelation temperature, ° C.	Appearance of gel immediately after cooling.	Time after which syneresis was observed.
2	53	Viscous stringy gel	3-4 weeks
4	51	Tough elastic gel	3-4 weeks
5	50	Very tough, elastic gel	3-4 weeks
6	50	Very tough, elastic gel	3-4 weeks
8	45	Very tough, elastic gel	3-4 weeks

The gel containing 2 per cent of soap exhibited viscous, stringy properties for about 2 weeks; the viscosity then decreased considerably and after 3 to 4 weeks the gel changed to a thin, soft grease and syneresis occurred. The other gels were tough, elastic, and non-sticky. In the most concentrated gels opaque white streaks appeared after 2 days; as illustrated in Fig. 6, these gradually spread irregularly throughout the gels, and after 3 to 4 weeks cracks developed along the streaks and became filled with clear liquid. Syneresis in each case was accompanied by a change to a grease which was, in general, thinner and smoother than the corresponding petrol product.

cycloHexene.

Gels were made with three samples of *cyclohexene*, as follows :

(i) Material as received; this contained a relatively large proportion of polymerized material (*ca* 3 per cent) and had a high peroxide value (0.70 g active oxygen/litre solvent);

(ii) Similar to (i) but washed with sodium bisulphite to remove peroxides; the peroxide content of the sample used was equivalent to 0.016 g active oxygen/litre solvent;

(iii) This sample was prepared by washing the original sample to remove peroxides, distilling to remove polymerized material and washing again to yield a product having a peroxide content equivalent to 0.012 g active oxygen/litre solvent.

TABLE IV.

Gelation in cycloHexene without Peptisers.

Sample of cyclohexene used.	Concentration of al. stearate, g/100 ml cyclohexene.	Gelation temperature, ° C.	Appearance of gel immediately after cooling.	Time after which syneresis was observed.
(i)	5	43	Moderately viscous gel	No syneresis observed after 3 months
(ii)	5	44	Slightly stringy, tough gel	
(iii)	2	47	Thin fluid gel	
(iii)	4	46	Slightly stringy, tough gel	
(iii)	5	45	Very tough gel	

The gels were practically transparent and possessed stringy, viscous properties. Comparison on the basis of mixtures containing 5 per cent of soap showed little difference in viscosity and stability between gels prepared from samples (ii) and (iii), but the unwashed *cyclohexene* gave a gel which was much less viscous and showed a more rapid loss of viscosity on prolonged storage. The presence of high-boiling polymerized material thus had relatively little effect in comparison with that due to peroxide.

The effect of variation in soap concentration was examined with the peroxide- and polymer-free solvent (Sample iii); the mixture containing 2 per cent of soap showed most rapid loss of viscosity. In the gels containing high soap concentrations, this phenomenon was less marked, but the loss of viscosity was none the less considerable and readily seen. In none of the gels was syneresis or structural breakdown observed over a period of 3 months.

Benzene.

TABLE V.

Gelation in Benzene without Peptisers.

Concentration of al. stearate, g/100 ml benzene.	Gelation temperature, ° C.	Appearance of gel immediately after cooling.	Time after which syneresis was observed.
2	47	Very thin gel	No syneresis observed after 3 months
4	45	Thick stringy gel	
5	45	Very thick gel	
6	44	Very thick gel	
8	43	Almost rigid, tough gel	

The gels in benzene were all water clear and varied in consistency from a very thin fluid gel to a tough elastic gel. They were the most stable of any of the gels prepared and showed the smallest changes in viscosity during storage.

The mixture containing 2 per cent of soap was a weak free-flowing gel, the viscosity of which gradually fell and, after 3 months, was little higher

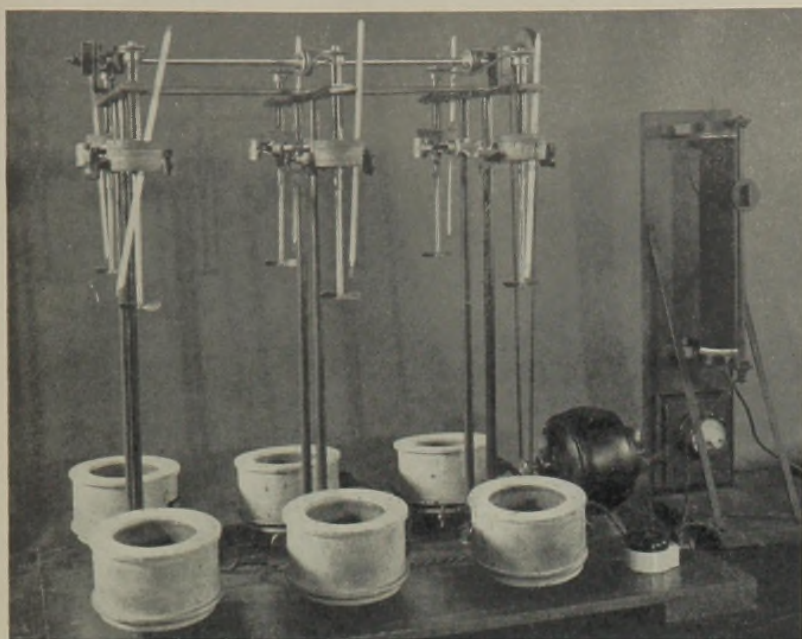


FIG. 1.
LABORATORY APPARATUS FOR THE PREPARATION OF GELS.

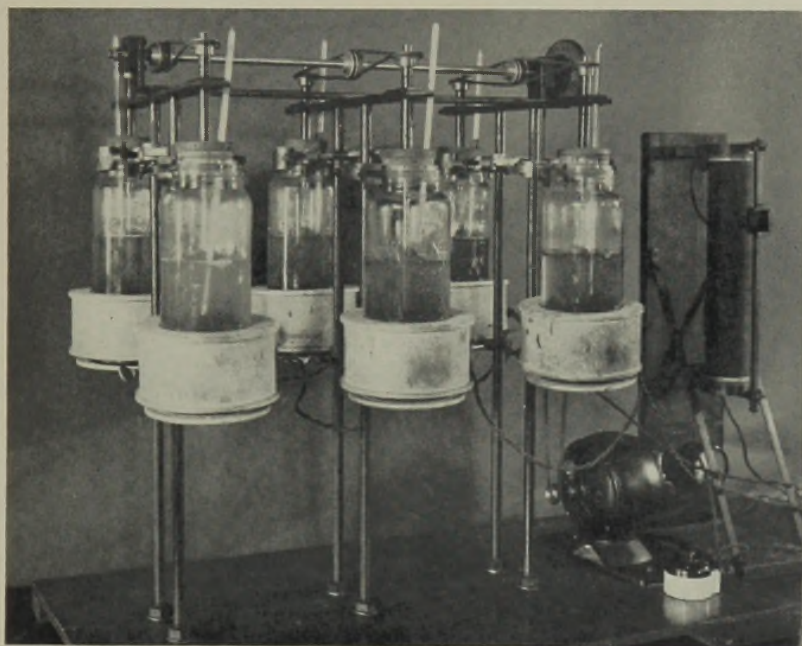


FIG. 2.
LABORATORY APPARATUS SHOWING SIX SAMPLES IN COURSE OF PREPARATION.

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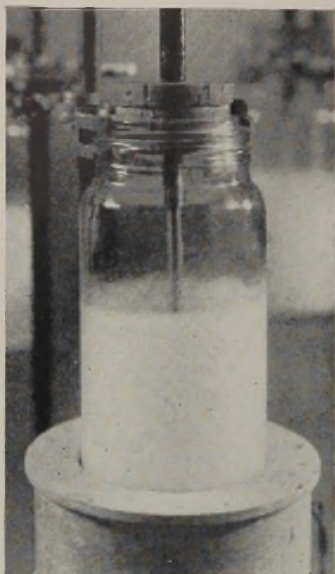


FIG. 3.
PREPARATION OF ALUMINIUM
STEARATE GEL: BEFORE GELA-
TION.



FIG. 4.
PREPARATION OF ALUMINIUM
STEARATE GEL: GELATION
BEGINS.

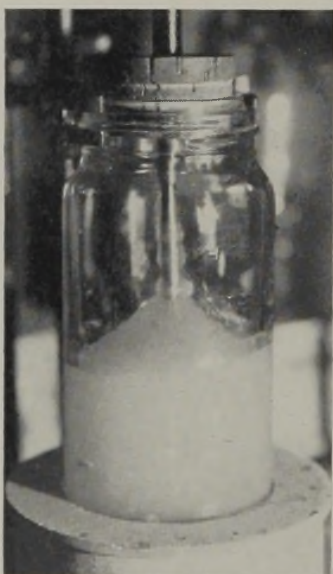


FIG. 5.
PREPARATION OF ALUMINIUM
STEARATE GEL: GELATION
COMPLETE.

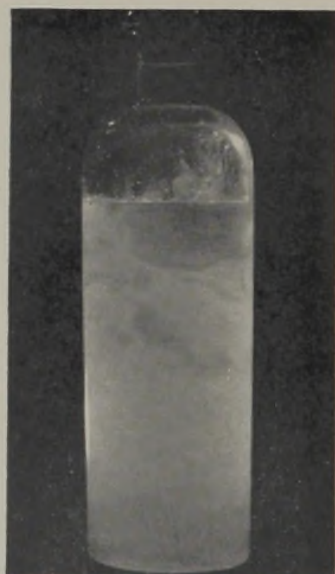


FIG. 6.
INCIPIENT BREAKDOWN IN UN-
PEPTISED ALUMINIUM STEARATE
GEL.

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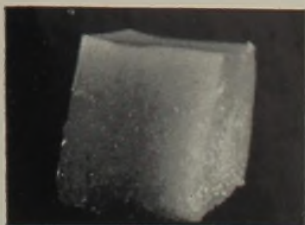


FIG. 10.
VISCIOUS FLOW OF SEMI-SOLID
GEL : AFTER 2 MINUTES.

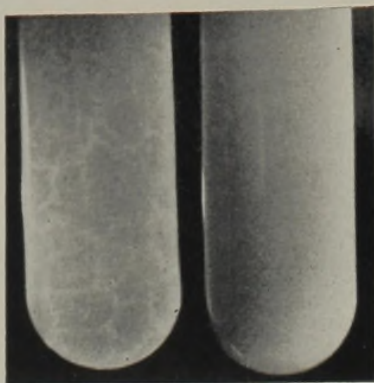


FIG. 15.
TEMPORARY BREAKDOWN IN GEL (ON
LEFT) ON COOLING.



FIG. 11.
VISCIOUS FLOW OF SEMI-SOLID
GEL : AFTER 30 MINUTES.

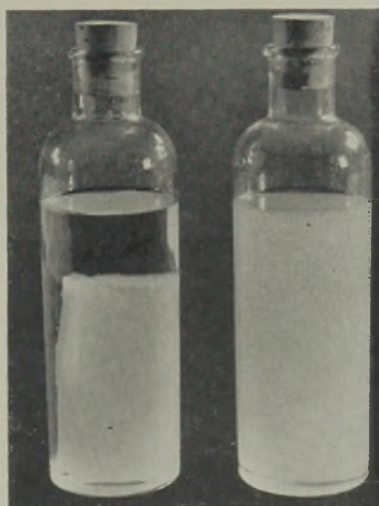


FIG. 16.
APPEARANCE OF UNPEPTISED AND
PEPTISED GELS AFTER COOLING.



FIG. 12.
VISCIOUS FLOW OF SEMI-SOLID GEL :
AFTER 2 HOURS.

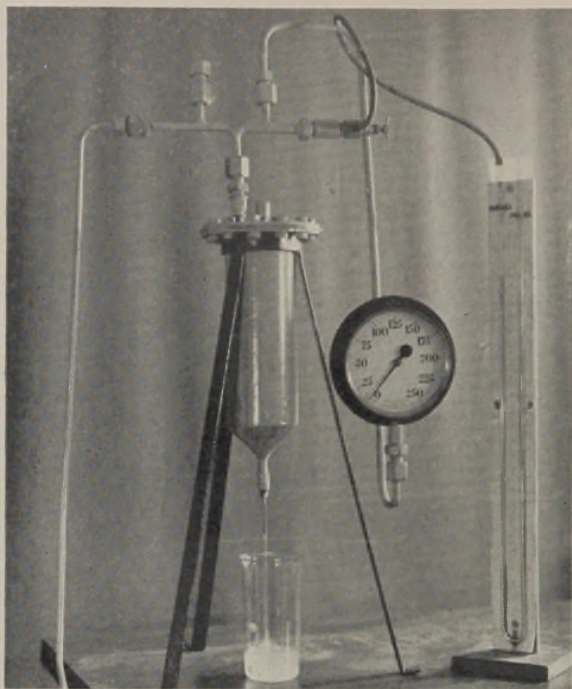


FIG. 18.
CAPILLARY-FLOW VISCOMETER.

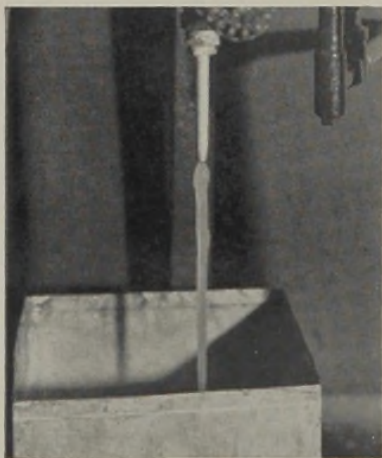


FIG. 21.
EXPANSION OF JET ON EMERGING FROM
A NOZZLE.

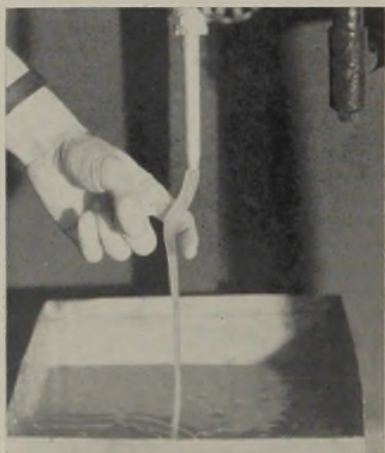


FIG. 22.
DISPLACEMENT OF A JET OF GEL.

than that of the original benzene. With increase in soap concentration, the viscosity of the gels increased, and the rate of loss of viscosity was much reduced; no decrease in viscosity could be observed with the gel containing 8 per cent of soap.

All the gels, however, showed structural breakdown after storage for 24 hours at a temperature of -5°C . On warming to room temperature after this treatment, syneresis occurred; the two phases consisted of benzene and a broken, grease-like translucent paste.

Summary.

Aluminium stearate was readily dispersed in benzene to give water-clear gels which increased in viscosity with increase in soap concentration. They exhibited good stability when stored at ordinary temperature, but rapidly showed structural breakdown at low temperature.

Similar results were obtained using *cyclohexene*, except that the gels showed a rapid rate of loss of viscosity, particularly when the peroxide content of the *cyclohexene* was high. The soap was less readily dispersed in *cyclohexane*, the gelation temperature being higher and the gels less stable. The gelation temperature was highest, and the gels least stable in paraffinic solvents. Gelation temperature, in all solvents, was lowered by an increase in the soap concentration.

Effect of Peptisers in Gelation.

Owing to their consistency and structural instability, aluminium stearate gels prepared without the addition of peptisers were unsuitable for purposes requiring free-flowing viscous liquids. It was found that the addition of relatively small quantities of certain substances not only influenced the gelation temperature and the gel consistency, but also profoundly modified the stability of the gels. By suitable choice of the added substance and the amount used, the gels could be broken down very rapidly, and in extreme cases gelation was inhibited completely. On the other hand, this "peptising" action could be controlled so as to modify the viscosity of the gels as desired and greatly to increase their stability. These effects are illustrated by the following results.

Gels in Petrol.

The results recorded in Table VI give some indication of the nature and magnitude of the effect of peptisers in petrol gels containing 5 per cent of aluminium stearate (5g/100 ml petrol).

The temperature of gelation varied somewhat with different peptisers, being lowest with mixed xlenols. The lower alcohols possessed such a marked peptising action that only very small additions were necessary to give suitable gel viscosities.

The nature and stability of the gels varied greatly with the different peptisers. Xlenols gave a viscous, stringy, sticky gel which did not show any structural change on prolonged storage at laboratory temperature; the rate of reduction in the viscosity of gels peptised with the alcohols was, however, considerable. Ethyl cellosolve gave a viscous, stable gel which

was more tough and elastic than that obtained with xylenols.* Cetyl alcohol gave a tough, rubbery gel which started to break down after 2 weeks; after about a month it had lost all stringiness and was a thick

TABLE VI.
Effect of Peptisers on Gelation in Petrol.

Peptiser.	Amount, g/100 ml. petrol.	Gelation temperature, ° C.	" Ball-drop " viscosity at 25° C after 1 day, sec.
None	—	57	∞
Mixed xylenols	1.5	45	170
Ethyl cellosolve	1.5	53	410
Oleic acid	1.5	53	2000
Acetone	1.5	57	∞
Methyl alcohol	0.3	54.5	85
Ethyl alcohol	0.3	54	105
<i>n</i> -Propyl alcohol	0.3	55	150
<i>n</i> -Butyl alcohol	0.3	55.5	205
Cetyl alcohol	1.5	57	200
Pyridine	0.2	56.5	∞

grease showing slight syneresis. The gels peptised with oleic acid rapidly lost viscosity, and acetone and pyridine both gave products which were grease-like and showed syneresis within 1 month.

Peptising Action of Phenols.

The effect of mixed xylenols in lowering the gelation temperature and in producing a stable, free-flowing, viscous gel, led to a closer examination of the action of various phenols as peptisers.

The results recorded in Table VII for mixtures containing 5 per cent of aluminium stearate and 1.5 per cent of peptiser showed that the peptising power of different phenols varied considerably. *o*-Cresol and 2 : 4- and 2 : 5-xylenol had a relatively weak action, while phenol was the most powerful peptiser.

TABLE VII.
Effect of Phenols on Gelation in Petrol.

Peptiser.	Gelation temperature, ° C.	" Ball-drop " viscosity at 25° C after 1 day, sec.
Phenol	37	100
<i>o</i> -Cresol	45	300
<i>m</i> -Cresol	45	145
<i>p</i> -Cresol	45	155
2 : 4-Xylenol	48	410
2 : 5-Xylenol	48	480
3 : 4-Xylenol	44.5	185
3 : 5-Xylenol	45.5	185

* Attention was first drawn by Dr H. G. Williams of the Anglo-American Oil Co. Ltd. to the interesting properties of ethyl cellosolve as a peptiser; these are not fully dealt with in this paper.

In general, the results indicated that there was a decrease in peptising power with each addition of a methyl group. Further, it appeared that the presence of a methyl group in a position *ortho* to the hydroxyl group had the greatest influence in reducing the peptising power of the phenol.

The relatively high peptising power of the commercial grade of mixed xylenols was known to be due, at least in part, to the presence of a small proportion of high boiling tar acids, but was possibly also partly due to the presence of small quantities of polyhydric phenols. An examination was therefore made of the peptising action of the three dihydroxyphenols and pyrogallol, and it was found that, except for hydroquinone, they exercised a marked peptising effect.

The solubilities of these phenols in petrol was so small that they were not suitable peptisers when used alone, and their action was examined in solution (2 per cent concentration) in 2:4-xylenol. Petrol gels were prepared using 5 per cent of soap and 1.5 per cent of mixed peptiser; the concentration of the polyhydric phenol in the gel was thus 0.03 per cent. The results are shown in Table VIII.

TABLE VIII.

Peptising Effect of Polyhydric Phenols.

Phenol added to 2:4-Xylenol.	Gelation temperature, ° C.	"Ball-drop" viscosity at 25° C after 1 day, sec.
No addition	48	410
Catechol	48	270
Resorcinol	48	325
Hydroquinone	50	450
Pyrogallol	48	145

The gelation temperature was practically unaffected and in all cases a viscous stringy gel was obtained. Pyrogallol was the most active peptiser and hydroquinone the least, and the peptising power appeared to increase with the number and proximity of the hydroxyl groups.

Gels in Various Solvents.

While approximate assessment of the effect of the nature of the solvent on gel quality was possible when no peptisers were employed, the addition of peptisers permitted more exact measurements to be made of viscosity and stability. Gels in several solvents were prepared, using 5 per cent of soap and respectively 1.5 per cent of mixed xylenols, 1.5 per cent of cellosolve, and 0.25 per cent of ethyl alcohol; the amount of ethyl alcohol was made relatively small so that it would give gels of the same order of viscosity as the other peptisers. The results are given in Table IX.

The results showed no consistent effect of the solvents on gel viscosity with the different peptisers. Similarly none of the peptisers showed the same effect in all the solvents, although the viscosities of the xylenols-peptised gels showed the least variation, and those of the cellosolve-peptised gels the most. Except for its behaviour in benzene, cellosolve showed the weakest action. It was evident that the effect of peptisers cannot be assessed from the examination of gels containing only a single arbitrarily-chosen concentration.

TABLE IX.

Effect of Solvent and Peptiser on Gelation.

Solvent.	Peptiser.	Gelation temperature, ° C.	"Ball-drop" viscosity at 25° C after 1 day, sec.
Petrol	Xylenols	45	170
	Cellosolve	52	400
	Alcohol	56	370
Benzene	Xylenols	42	230
	Cellosolve	44	85
	Alcohol	45	265
<i>cyclo</i> Hexane	Xylenols	38	175
	Cellosolve	46	650
	Alcohol	47	205
<i>cyclo</i> Hexene (Sample iii)	Xylenols	37	260
	Cellosolve	42	320
	Alcohol	42	220
Light petroleum (b.p. 80-100° C)	Xylenols	43	125
	Cellosolve	51	415
	Alcohol	56	75

Effect of Concentration of Peptisers. The effect of varying the concentration of mixed xylenols and cellosolve on the viscosity of gels containing 5 per cent of soap in various solvents is illustrated in Figs. 7 and 8.

In gels peptised with mixed xylenols (Fig. 7) the effect due to the solvent

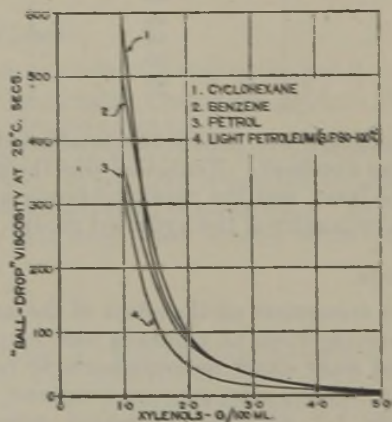


FIG. 7.

PEPTISING ACTION OF XYLENOLS IN DIFFERENT SOLVENTS.

was relatively small, but in general the most viscous gels were obtained in benzene and the least viscous gels in light petroleum.

The effect of small changes in the concentration of xylenols was high at low concentrations (up to 2 per cent) and relatively low at high concentrations. The gel containing 0.5 per cent of xylenols soon became more viscous and changed to a thick grease in which syneresis occurred within 2 months.

The lowering of the temperature of gelation, by an increase in the

concentration of xyenols was considerable in all solvents. It was greatest in the paraffinic solvents; an increase in the concentration of xyenols from 0.5 to 5.0 per cent reduced the gelling temperature from 54°C to 36°C in light petroleum, and from 44°C to 38°C in benzene.

When cellosolve was used as the peptiser (Fig. 8) the nature of the solvent had a much greater effect on gel viscosity. The gels were most viscous in light petroleum and least viscous in benzene, whereas this order was reversed in gels peptised by mixed xyenols.

The rate of change of viscosity with concentration of peptiser was in a

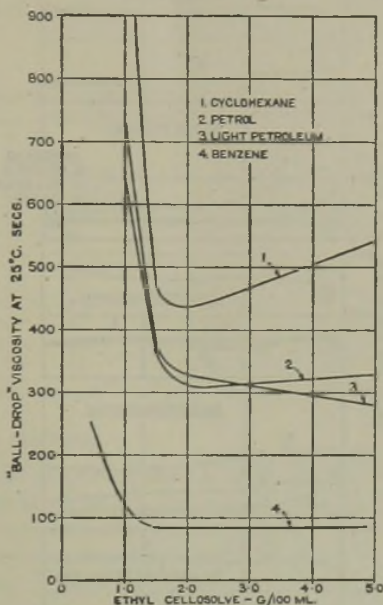


FIG. 8.

PEPTISING ACTION OF ETHYL CELLOSOLVE IN DIFFERENT SOLVENTS.

general way similar to that observed with xyenols; with concentrations above about 1.5 per cent the effect of the peptiser was either negligible or reversed. Thus with light petroleum an increase in the concentration of cellosolve up to 20 per cent (not shown in Fig. 8) had no appreciable influence on the viscosity of the gel.

Increase in the concentration of cellosolve had very little effect in reducing the gelling temperature; the maximum lowering, observed with light petroleum, was 5°C .

The peptising power of ethyl alcohol was very much greater than that of xyenols or cellosolve and, with gels containing 5 per cent of soap, variations from 0.1 to 0.3 per cent of peptiser produced changes in the "ball-drop" viscosity covering a large part of the practical range of measurement. Thus, with petrol, the gel viscosities at 0.1 and 0.3 per cent of alcohol were respectively 1400 and 105 seconds.

Stability of Peptised Gels.

Gels prepared in various solvents with 5 per cent of soap and respectively 1.5 per cent of mixed xylenols, 1.5 per cent of cellosolve and 0.25 per cent of alcohol were stored at laboratory temperatures (15 to 20° C) for 3 months and "ball-drop" viscosities were measured at intervals. The results are shown graphically in Fig. 9.

The gels peptised with xylenols or cellosolve were structurally stable,

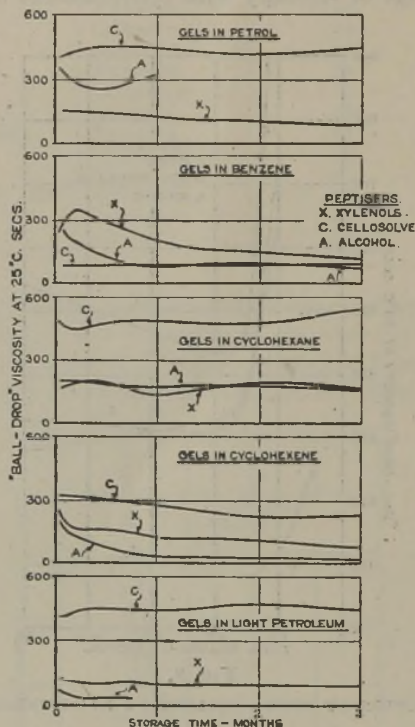


FIG. 9.

EFFECTS OF SOLVENTS AND PEPTISERS ON GEL STABILITY.

but there was a gradual lowering in viscosity when xylenols was the peptiser. There was not a large difference between the results obtained with different solvents although the saturated hydrocarbons gave gels of the greatest viscosity stability.

The alcohol-peptised gels showed a much lower stability. In petrol and light petroleum the viscosities of the gels at first decreased—for 1 or 2 weeks—and then gradually increased; the gels lost their initial sticky, stringy properties and gradually changed to greases which soon showed syneresis. On the other hand, gels in the other solvents all showed a gradual lowering of viscosity, the rate of change being most rapid in *cyclohexene* and least rapid in *cyclohexane*.

Effect of Concentration of Soap. A series of gels was prepared in petrol in which the amount of soap was varied from 2.0 to 8.0 per cent while the ratio of xlenols to soap was maintained at 0.3 : 1. The results are given in Table X and showed that an increase in the concentration of gelling agents led to an increase in the viscosity stability of the gels.

The viscosity of the gels also increased with the concentration of the soap. With 8 to 12 per cent of soap, semi-solid gels were obtained when the amount of the peptiser was small (about 1 per cent); when a mixed peptiser of xlenols and cellosolve was used, these semi-solid gels showed little change in viscosity over a period of 6 months. The viscous flow of gels of this type is illustrated by the photographs shown in Figs. 10, 11, and 12.

TABLE X.
Effect of Concentration of Aluminium Stearate.

Gel composition		Gelation temperature, ° C.	" Ball-drop " viscosity at 25° C after			
Aluminium stearate, g/100 ml.	Mixed xlenols, g/100 ml.		1 day, sec.	1 month, sec.	2 months, sec.	3 months, sec.
2.0	0.6	55	< 1	< 1	—	—
4.0	1.2	49	16	13	9	6
5.0	1.5	45	175	160	130	105
6.0	1.8	44	330	290	240	225
8.0	2.4	41	750	700	650	620

Effect of Moisture in the Soap.

Water is a powerful peptising agent, and the importance in practice of maintaining a constant moisture content of the soap is therefore evident, especially as aluminium stearate powder is hygroscopic. Water alone may be used to produce viscous free-flowing petrol gels with aluminium stearate, but they are unstable. Thus a gel prepared in petrol using 5.3 per cent of aluminium stearate having a moisture content of 6.3 per cent initially had almost the same viscosity as a gel made with 5 per cent of the same soap containing 1.5 per cent of moisture and peptised with 2 per cent of xlenols. The viscosity of the gel peptised with water alone, however, was reduced to about 10 per cent of its initial value in 48 hours; exposed to a temperature of 10° F for 18 hours, the same gel showed syneresis. The gel containing xlenols, on the other hand, showed no measurable change after similar treatments.

The powerful peptising action of water is illustrated graphically in Fig. 13 by the effect of varying moisture contents of the aluminium stearate on gels prepared in petrol with 5 per cent of soap and 1.5 per cent of mixed xlenols.

It was found that an increase in the moisture content of the soap tended to reduce the viscosity stability of the gels, but that the effect was comparatively small, at any rate for moisture contents up to about 2 per cent in gels of the type described, *i.e.*, in which the amount of xlenols is large in comparison with the amount of water. Where highly viscous gels are required, the importance of a low moisture content is evident, but very

dry soaps are extremely hygroscopic and their use introduces practical difficulties. It was found that a moisture content of 1.0 per cent was most generally satisfactory in practice.

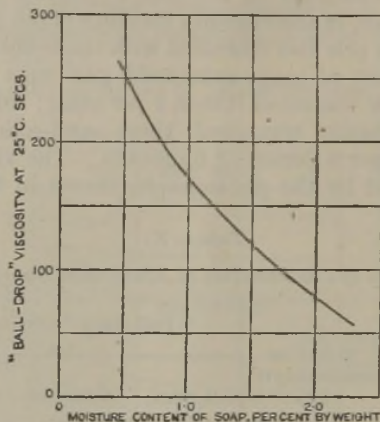


FIG. 13.

EFFECT ON GEL VISCOSITY OF MOISTURE CONTENT OF ALUMINIUM STEARATE.

Other Factors Affecting Gel Viscosity and Stability.

Effect of Temperature of Preparation of Gels.

Mixtures in petrol were prepared by the method described, using 5.5 per cent of aluminium stearate and 1.65 per cent of mixed xylenols, except that the maximum temperature of mixing was varied. In each case the mixture

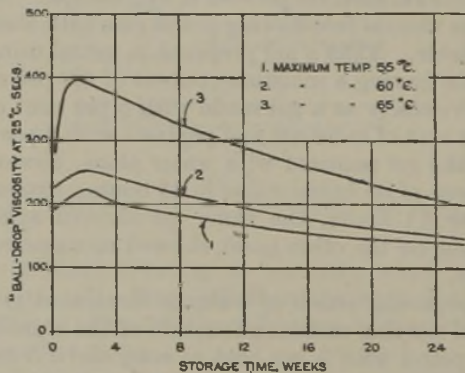


FIG. 14.

EFFECT OF TEMPERATURE OF PREPARATION ON GEL VISCOSITY.

was heated uniformly to the gelation temperature (44° C) in 30 minutes, and then to 50° C during a further 20 minutes. During a further 40 minutes heating mixtures were heated respectively to 55°, 60°, and 65° C. The results, recorded in Fig. 14, showed that a marked increase in viscosity

resulted from heating to 65° C. On storage, the rate of loss of viscosity was at first pronounced with gels prepared at the highest temperature, but after some weeks it gradually declined, so that all the gels approached a condition of similar viscosity. In these and other experiments with xyenols-peptised gels, it was in general found that the viscosity-stability of gels was greatest when the maximum temperature of preparation was about 10° C above the gelation temperature. When cellosolve was used as the peptiser, the viscosity of the gels was much more sensitive to the small variations in the temperature of preparation.

Effect of Storage Conditions.

The concentrations of aluminium stearate and peptiser used in the preparation of the peptised gels for which data are quoted in this section, were in all cases 5.0 and 1.5 per cent respectively.

Temperature. Although many of the gels possessed a high degree of viscosity-stability during storage at laboratory temperature, it was found that the rate of lowering of viscosity was accelerated at higher temperatures, and that gel stability was often affected at very low temperatures.

Gels in petrol, peptised with mixed xyenols, were stored for successive 7-day periods at 40° C and — 18° C (0° F) respectively; at the end of each period the samples were transferred to a bath at 25° C and after 2 days the "ball-drop" viscosity at 25° C was measured. The results are recorded in Table XI, together with comparative data for a similar gel stored at laboratory temperature (18 to 20° C). The gels showed good viscosity stability at — 18° C, but at 40° C the decrease in viscosity was considerable. In general it was found that aluminium stearate petrol gels peptised with xyenols were very stable at low temperatures, but underwent a gradual increase in rate of lowering of viscosity as the temperature was raised.

The stability of a similar gel at very low temperature was examined in a separate series of experiments. Samples in glass tubes were immersed in an

TABLE XI.

Effect of Temperature of Storage on Gel Viscosity.

Storage temperature, ° C.	"Ball-drop" viscosity at 25° C.					
	Initial, sec.	After storage for				
		1 week, sec.	2 weeks, sec.	3 weeks, sec.	4 weeks, sec.	2 months, sec.
40	185	115	75	55	45	20
—18	185	175	180	170	170	140
18–20	185	170	—	160	155	130

alcohol bath cooled by means of solid carbon dioxide. Temperatures were measured in the gel and the bath; the temperature was lowered from 0° C to —77° C in a period of 4 to 5 hours, and the rate of cooling was adjusted so that the difference between the temperatures of the gel and the bath was negligible.

The viscosity of the gel increased as the temperature was lowered. At

temperatures down to -30°C the gel was mobile and stringy; at -32°C a marked change occurred, all stringiness and mobility disappeared, and the gel became tougher and rubbery and somewhat brittle, and showed a slight tendency to fracture. Further cooling to -45°C caused an increase in rigidity and brittleness, and the gel started to shrink. Syneresis was first observed at a temperature of -45°C and became more pronounced as the temperature was lowered. At -64°C cracks appeared and gradually developed throughout the gel. At a temperature of -77°C the syneresis had occurred to such an extent that the solvent had filled the cracks and covered the surface of the gel. The appearance of the gel at this stage, compared with that of the original gel, is illustrated in Fig. 15.

When the gel was allowed to warm up to laboratory temperature the solvent which had separated was reabsorbed, and the gel regained its stringy properties. The viscosity of the gel reached a constant value after 3 to 4 days at 25°C , and showed a small reduction from its original value, i.e., 225 seconds as against 245 seconds.

When an unpeptised gel containing 5 per cent of aluminium stearate was cooled to 0°C structural breakdown occurred rapidly. Syneresis occurred after 30 minutes at this temperature and this change proved to be irreversible. The appearance of the gel after 3 to 4 hours at 0°C is shown photographically in Fig. 16 in comparison with that of a gel peptised with 1.5 per cent of mixed xylenols, after storage for one month at -18°C (0°F).

Exposure to Light. The viscosities of the gels were observed to fall more rapidly during storage when the gels were exposed to daylight. This effect is illustrated by the results given in Table XII for a gel prepared in petrol, peptised with mixed xylenols.

TABLE XII.

Effect of Exposure to Light on Gel Viscosity.

Storage conditions.	"Ball-drop" viscosity at 25°C after storage for			
	1 day, sec.	1 week, sec.	3 weeks, sec.	4 weeks, sec.
Light	170	165	125	100
Dark	170	170	145	135

In general this effect was more pronounced with petrols containing higher proportions of unsaturated hydrocarbons, suggesting that the formation of organic peroxides accelerated the reduction in viscosity. The removal of peroxides from petrols by washing with sodium bisulphite was found to increase the viscosity stability of the gels, and the effect was more marked with aged petrols having a high peroxide content. The effect of removal of peroxides is shown by the results given in Table XIII.

Peroxide removal also increased the initial viscosity of the gels, but the rate of lowering of the viscosity was still appreciable with gels prepared from washed petrol, indicating that peroxides were probably not responsible for the whole effect.

Similar conclusions were reached as the result of an examination of xylenols-peptised gels prepared in cyclohexene (Table XIV), but when

TABLE XIII.

Effect of Peroxides on Gel Viscosity.

Petrol.	Peroxide content, (active O ₂ , g/litre).	" Ball-drop " viscosity at 25° C after		
		1 day, sec.	1 week, sec.	3 weeks, sec.
1	0.012	170	160	140
	0.002	170	185	165
2 (aged)	0.432	20	15	10
	0.004	90	82	62

TABLE XIV.

Effect of Peroxide Content of cycloHexene on Gel Viscosity.

Peroxide content, (active O ₂ , g/litre).	Peptiser.	" Ball-drop " viscosity at 25° C after		
		1 day, sec.	1 month, sec.	3 months, sec.
0.70	Xylenols	42	9	2
0.016		145	88	38
0.70	Cellosolve	255	205	185
0.016		355	340	345

cellosolve was used as the peptiser the viscosity stability of the gels was of a much higher order.

Size and Nature of Container. The samples examined in the course of this work were all stored in glass, although they were not exposed to daylight except where specifically stated. It was found that the presence of copper and lead had a large, and zinc a small, effect in increasing the rate of

TABLE XV.

Effect of Size and Nature of Container on Storage Stability.

Sample.	" Ball-drop " viscosity at 25° C after				
	1 day, sec.	7 days, sec.	60 days, sec.	90 days, sec.	120 days, sec.
8 gallons in iron drum	160	185	—	175	170
360 ml in glass bottle	160	155	120	85	60

reduction in viscosity of gel peptised with xylenols. On the other hand, iron and tin had no deleterious effect, so that in view of the influence of daylight, storage in iron drums or tinned-iron cans was less harmful than storage in glass.

Another observation, often confirmed but never fully explained, was that gels maintained their viscosity much better when stored in bulk. Gels stored in drums (5 to 50 gallons capacity) have invariably proved to be much more stable than those for which results have been quoted in this paper. This is illustrated by results recorded in Table XV for a sample of

8 gallons of a petrol gel, peptised with mixed xylenols, stored in an iron drum in comparison with viscosities of a small sample (360 ml) of the same gel stored in glass. The greater stability of the larger sample is marked, but it is uncertain whether this was due to the effect of the metal or to the relatively smaller surface area compared with the glass-contained sample.

Properties of Aluminium Stearate Gels.

The means by which the viscosity and stability of aluminium stearate gels may be influenced by varying the concentration of soap and the nature and concentration of the peptiser have already been indicated. In this section a description is given of some of the properties of petrol gels in which xylenols was used as the peptiser.

Anomalous Viscosity.

Petrol gels made from aluminium stearate peptised with xylenols superficially resemble the viscous solutions of rubber in hydrocarbon solvents. They also resemble these solutions in showing the property of anomalous viscosity, the apparent viscosity decreasing with increasing rate of shear.

This property was demonstrated and measured in a capillary tube viscometer which is illustrated diagrammatically in Fig. 17; a photograph

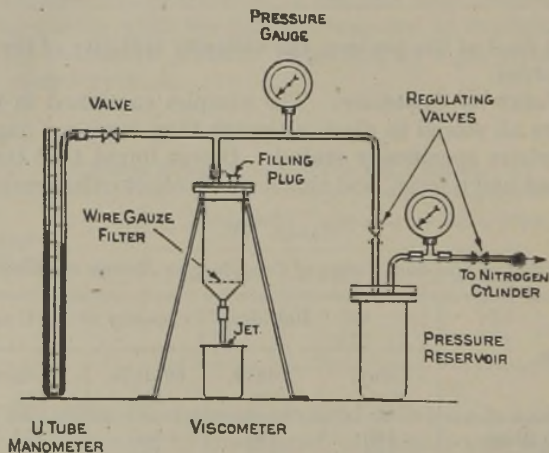


FIG. 17.

CAPILLARY-FLOW VISCOMETER.

of the actual apparatus is shown in Fig. 18. The viscometer consisted of a cylindrical steel vessel with a conical base into which was screwed a plug carrying the capillary tube, made of steel pressure tubing 3 inches long to 1/16 inch nominal bore. The vessel was connected by steel pressure tubing to a mercury U-tube manometer for pressures up to about 1 atm, a dial pressure gauge for higher pressures, and through a pressure balancing reservoir to a cylinder of nitrogen. The method of experiment was to determine the volume of efflux at a known pressure over a measured time,

the apparatus having been calibrated by use of a Newtonian fluid (a commercial lubricating oil) of known viscosity.

Using the normal Poiseuille equation (with the appropriate correction for the kinetic energy of the fluid leaving the jet and the Couette correction) the apparent viscosity was determined as a function of the apparent rate of shear, as determined by the formula used for Newtonian liquids.

The results obtained by this apparatus are illustrated in Fig. 19 by the curves for three fuels of "ball-drop" viscosities ranging from 1 to 47 seconds. All the fuels exhibited marked anomalous viscosity, the apparent

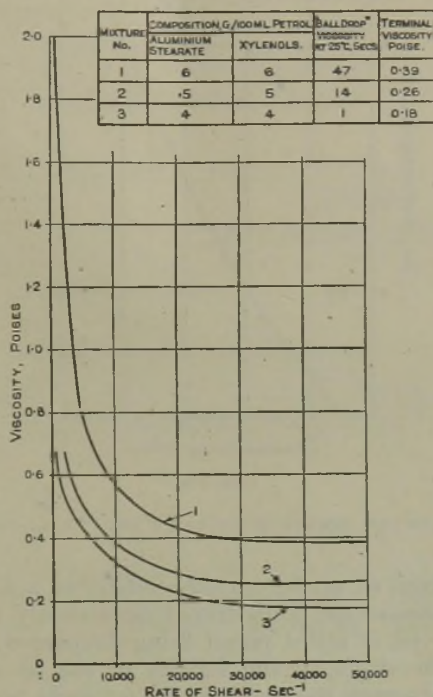


FIG. 19.

EFFECT OF RATE OF SHEAR ON GEL VISCOSITY.

viscosity decreasing greatly with increasing rate of shear; the limiting value of the viscosity obtained at high rates of shear ("terminal viscosity") ranged from 0.18 to 0.39 poises as compared with the values of 10 to 470 poises (*i.e.*, 1 to 47 seconds) obtained at low rates of shear by the "ball-drop" method.

It was thought that the "terminal viscosity" might be of greater value in characterizing the gels than the "ball-drop" viscosity. It was found, however, as a result of a large number of experiments with fuels of widely different compositions and viscosities, that gels placed in a certain order according to "terminal viscosity" were, in general, placed in the same order by "ball-drop" viscosity (Fig. 20). Since the terminal viscosity

therefore appeared to have no special significance, it was concluded that the simple "ball-drop" method would provide a reasonably adequate assessment of the viscosity of the gels.

In the photograph of the viscometer (Fig. 18) the shape of the jet of gel leaving the capillary tube is of particular interest. The expansion of the

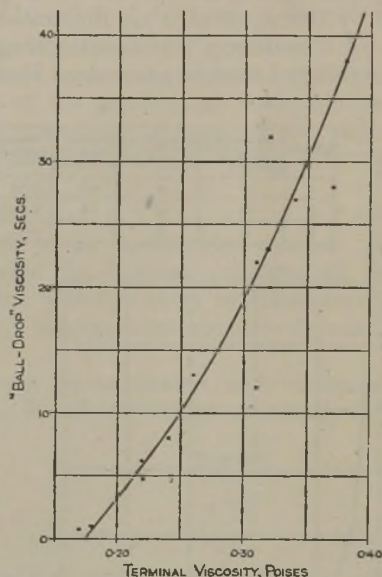


FIG. 20.

RELATIONSHIP BETWEEN TERMINAL VISCOSITY AND "BALL-DROP" VISCOSITY.

jet on emerging from an orifice is characteristic of a fuel of anomalous viscosity; this phenomenon is illustrated more clearly in Fig. 21 by the photograph of the jet of gelled petrol being discharged from an 8-gallon mixing vessel. The elasticity and rigidity of the jet are illustrated in Fig. 22 by the photograph showing how the jet could be deflected without wetting the finger.

Temperature Sensitivity.

Most of the aluminium stearate gels examined had a high temperature sensitivity—that is, the viscosity increased rapidly with fall in temperature. The temperature sensitivity was found to increase with increase in the soap concentration, but was most affected by the nature and amount of the peptiser. In general, gels of lower viscosity showed a smaller sensitivity.

The effects on the temperature sensitivity of peptising gels in petrol containing 5 per cent of aluminium stearate with xylenols, cellosolve, and alcohol are shown graphically in Fig. 23. Gels peptised with cellosolve had a much greater temperature sensitivity than gels peptised with xylenols, having similar "ball-drop" viscosities at 25° C. The use of alcohol as a peptiser gave a greatly reduced temperature sensitivity, and as

shown in Fig. 23, this feature was still apparent when mixtures of peptisers were used, addition of alcohol to either xylenols or cellosolve resulting in a reduced temperature sensitivity in each case.

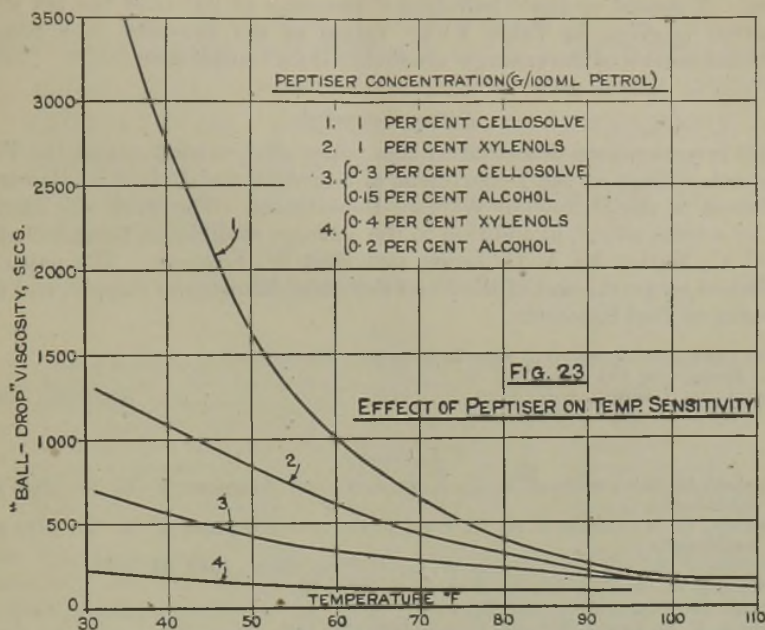


FIG. 23.

Mechanical Stability.

Peptised aluminium stearate gels were found to possess a very high degree of mechanical stability, that is to say they could suffer a violent mechanical disturbance without showing any signs of structural breakdown

TABLE XVI.

Effect of Agitation on Gel Viscosity.

	Sample 1 stirred.	Sample 2 not stirred.
Initial value of "ball-drop" viscosity, sec	170	170
"Ball-drop" viscosity immediately after stirring, sec :	157	—
After 10 minutes	156	—
After 60 "	156	170
After 75 "	159	170
After 160 "	161	169
After 24 hours	167	169

or undergoing any appreciable permanent reduction of viscosity. When pumped by means of a gear pump, or otherwise subjected to mechanical disturbance, the gels showed a small thixotropic effect; the viscosity was lowered to a small extent but gradually returned to its original value during

the course of a few hours. This effect was illustrated by the behaviour of a sample of gel immediately after being subjected to vigorous mechanical agitation for 10 minutes by means of two-bladed stirrer revolving at 1500 r.p.m. A record of the "ball-drop" viscosity at 25° C of the gel after agitation is given in Table XVI; values of the viscosity of a second unstirred sample of the same gel are included for comparison.

Acknowledgment.

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THE EXTREME PRESSURE (E.P.) LUBRICATING PROPERTIES OF SOME BROMINE AND IODINE COMPOUNDS, ALONE AND IN PRESENCE OF SULPHUR, WITH OBSERVATIONS ON THE MECHANISM OF THE DEVELOPMENT OF E.P. PROPERTIES.

By W. DAVEY, B.Sc., Ph.D., F.R.I.C.

SUMMARY.

Certain bromine and iodine compounds show E.P. properties when blended in mineral oil. The bromine compounds are markedly superior to the corresponding chlorine compounds, whilst the iodine compounds are inferior to both bromine and chlorine compounds in E.P. properties on the results of tests on the four ball machine. The E.P. properties of blends of bromine and iodine compounds are greatly improved by the addition of reactive sulphur. The mechanism of action of bromine and iodine compounds as E.P. additives has been shown to be similar to that of chlorine compounds.

It has been shown¹ that certain chlorine compounds, blended in mineral oil, show marked E.P. properties and that^{2,3} the addition of reactive sulphur appreciably improves the E.P. properties of these blends. Such chlorine compounds react with iron to form ferrous chloride films and the formation of such films is essential under extreme pressure conditions. The addition of reactive sulphur improves the E.P. properties of a chlorine compound by facilitating the formation of the ferrous chloride film, ferrous sulphide being formed in the reaction. As far as the present author is aware no information has been published on the E.P. properties of bromine and iodine compounds and the present work gives a comparison between the E.P. properties of chlorine, bromine, and iodine compounds.

Blends of certain bromine and iodine compounds, in Genuine Penna 150 Neutral Oil, have been tested in the four ball machine, and the results obtained indicate that bromine compounds are superior to chlorine compounds as E.P. additives, whilst iodine compounds are inferior. In the case of iodine compounds relatively few compounds were tested, since many of them, *e.g.*, iodoform, carbon tetra-iodide, had too low a solubility in the oil to permit tests to be made.

The addition of reactive sulphur improves the E.P. properties of bromine and iodine compounds and the sulphur acts in the same manner as in the case of chlorine compounds. Evidence has been obtained that, in certain cases, addition compounds may be formed by the ferrous sulphide film and the halogen compound and also by the reactive sulphur compound and the halogen compound. The method of pre-forming films on the test balls, used to elucidate the mechanism of action of chlorine compounds and sulphur, has been used to study the mode of action of bromine and iodine compounds and their action shown to be similar.

EXPERIMENTAL

10, 5, and 1 per cent weight blends of the bromine and iodine compounds in Genuine Penna 150 Neutral Oil were prepared and tested in the four ball machine, the standard short duration test being used throughout. The results obtained are given below in tabular form, the proposed new method of presentation⁴ being used, and the results obtained for corresponding chlorine compounds are included for purposes of comparison.

TABLE I.

The E.P. Properties of Chlorine, Bromine, and Iodine Compounds.

Compound or blend tested	Wear-load ratio, kg/mm	Maximum load, kg.	Type of curve	Friction-time curves.	
				Seizure	Frictional torque
10% wt blends of:					
Chlorinated paraffin wax	220/<210 kg 50/210-270 kg 200/>270 kg	Welding at 410	D	Instant	Low—rapid recovery
Brominated paraffin wax	357	Tested to 300	D	"	"
Bromobenzene	76	Tested to 150	D	"	High—seizure prolonged
Iodobenzene	76	" "	D	"	"
p-Dichlorobenzene	50	Tested to 120	D	"	"
p-Dibromobenzene	76	Tested to 150	D	"	"
Methyl iodide	144	" "	D	"	"
iso-Propyl iodide	74	" "	D	"	"
n-Butyl iodide	72	" "	D	"	"
Methylene di-iodide	106	Tested to 400	D	"	Low—rapid recovery
Chloroform	24/170-200 kg 200/>200 kg	Welding at 410	D	"	High—fairly rapid recovery
Bromoform	270	Tested to 500	D	"	Low—rapid recovery
Carbon tetrachloride	250/<280 kg 56/280-330 kg 250/>330 kg	Slight welding at 410	D	"	"
Carbon tetrabromide	500	Tested to 500	D	"	"
Tetrachloroethane	220/<210 kg 36/210-270 kg 200/>270 kg	Welding at 410	D	"	High—fairly rapid recovery
Tetrabromoethane	72	Tested to 400	D	"	High—rapid recovery
Benzyl chloride	300	Tested to 410	D	"	Low—instant re-
Benzyl bromide	200	Tested to 300	D	"	Low—rapid recovery
5% wt blends of:					
Methyl iodide	143	Tested to 150	D	Instant	High—rapid recovery
Methylene di-iodide	125	Tested to 300	D	"	"
Chloroform	120	Slight welding at 300	D	"	"
Bromoform	125	Tested to 400	D	"	"
Tetrabromoethane	154	Tested to 300	D	"	"
Carbon tetrachloride	40/<200 kg 250/>200 kg	Slight welding at 410	D	"	"
Carbon tetrabromide	400	Tested to 500	D	"	"
Benzyl chloride	40/<200 kg 330/>200 kg	Slight welding at 410	D	"	"
Benzyl bromide	125	Tested to 300	D	"	"
1% wt blends of:					
Iodine	500	Tested to 300	D	Instant	Very low torque almost instant recovery
Methylene di-iodide	126	Tested to 250	"	"	High—rapid recovery
Tetrabromethane	76	Tested to 300	"	"	"
Carbon tetrachloride	144	Welding at 410	"	"	"
Carbon tetrabromide	220	Tested to 300	"	"	"
Chloroform	120	Welding at 300	"	"	"
Bromoform	168	Tested to 250	"	"	"
Benzyl chloride	182	Welding at 310	"	"	"
Benzyl bromide	125	Tested to 200	"	"	"

In order to study the effect of the addition of sulphur on the E.P. properties of bromine and iodine compounds, blends of 5 per cent wt of the bromine or iodine compound and 0.6 per cent wt of sulphur were prepared and tested. The results obtained are given below :—

TABLE II.

The Effect of Added Sulphur on the E.P. Properties of Bromine and Iodine Compounds.

Compound or blend tested	Wear-load ratio, kg/mm	Maximum load tested, kg	Type of Curve	Friction-time curves.	
				Seizure	Frictional torque
0.6 wt sulphur	333	300	C	No seizure	Low—smooth wear throughout
0.6% wt sulphur + 5% wt methyl iodide	167	250			
0.6% wt sulphur + 5% wt ethyl bromide	400	400			
0.6% wt sulphur + 5% wt methylene di-iodide	333	300			
0.6% wt sulphur + 5% wt tetrabromoethane	333	400	D	Instant	Low—rapid recovery
0.6% wt sulphur + 5% wt bromoform	500	400			
0.6% wt sulphur + 5% wt carbon tetra-bromide	665	400			

In order to investigate the mechanism of action of bromine and iodine compounds as E.P. additives, ferrous bromide films and ferrous bromide-ferrous sulphide films were prepared on test balls by passing dry hydrogen bromide over oil-free test balls and over test balls coated with ferrous sulphide respectively. Similar ferrous iodide films were prepared by passing iodine vapour over test balls and over sulphide-coated test balls. These coated test balls were then tested using Genuine Penna 150 Neutral Oil as lubricant and the results are given below :—

TABLE III.

Effect of Pre-formed Films.

Nature of film	Wear-load ratio, kg/mm	Maximum load tested, kg	Type of curve	Friction-time curves	
				Seizure	Frictional torque
Ferrous bromide	166	200*	D	Instant	Low—rapid recovery
Ferrous bromide-ferrous sulphide	122	200*			
Ferrous iodide	83	200*			
Ferrous iodide-ferrous sulphide	71	200*			

* Welding at 300.

The results of tests on chlorine compounds and reactive sulphur in mineral oil have indicated that addition compounds may be formed by

the ferrous sulphide film, formed by the reactive sulphur, and the chlorine compound, and this suggestion has, to some extent, been confirmed by the action of such chlorine compounds on ferrous sulphide films.^{2, 3} A similar mechanism appears to operate with bromine and iodine compounds, since on passing a solution of a bromine or iodine compound in petroleum ether through a layer of ferrous sulphide the bromine or iodine compound becomes attached to the ferrous sulphide and cannot be removed by washing with the solvent, indicating that the process is not one of simple adsorption. It is hoped to investigate the nature of these addition products by X-ray methods in the near future.

The formation of sulphonium salts by halogens and halogen compounds and sulphides or disulphides is well known and it was thought that such compounds might be formed from active sulphur compounds and halogen compounds showing E.P. properties. This has been confirmed by tests using diethyl sulphide and bromine compounds. Diethyl sulphide does not react readily to form a ferrous sulphide film with iron surfaces, but becomes active in presence of bromine compounds. Furthermore, a blend of diethyl sulphide and ethyl bromide yielded a crystalline deposit of the sulphonium salt on cooling to 0°C. It must be pointed out that these compounds are not formed as readily by chlorine compounds, but the formation of such salts may be important in the development of E.P. properties by blends of chlorine and sulphur compounds. That such compounds are formed appears probable in view of the enhanced E.P. properties shown when chlorine and sulphur are combined in a single additive.⁵

The results of the tests on diethyl sulphide and bromine compounds are given below :—

TABLE IV.
E.P. Properties of Diethyl Sulphide and Bromine Compounds.

Compound or blend tested	Wear-load ratio, kg/mm	Maximum load tested, kg	Type of curve	Friction-time curves	
				Seizure	Frictional torque
1% wt diethyl sulphide	119	150	D	Instant	High—recovery somewhat delayed
+ 1% wt ethyl bromide	50	200	D	Instant	Low—rapid recovery
+ 1% wt bromoform	56	200			
+ 1% wt carbon tetrabromide	167	200			

DISCUSSION OF RESULTS.

The results obtained show the marked superiority of bromine compounds as E.P. additives over chlorine and iodine compounds. In general, bromine compounds show a much higher wear-load ratio than the corresponding chlorine or iodine compounds and impart a higher load bearing capacity to the oil. The friction-time curves obtained for bromine compounds were excellent examples of the D type of curve, and this type of curve

has been found to be characteristic of the most effective E.P. lubricants. Even in the case of bromobenzene and *p*-dibromobenzene the bromine atoms are more reactive than in the case of *p*-dichlorobenzene. In the case of benzyl bromide the bromine atom is very easily split out by water and this may account for the higher wear shown by blends in comparison with benzyl chloride. In spite of the superior E.P. properties of bromine compounds they are unlikely to be employed commercially owing to the present high cost of bromine in comparison with chlorine.

The few iodine compounds tested show inferior E.P. properties and a high percentage of iodine in a compound is required to produce appreciable E.P. effects. The results on iodine compounds are thus only of academic interest owing to the large amount of compound required for effective E.P. lubrication and to the prohibitive cost of iodine compounds.

The work on the effect of added sulphur and the study of the mode of action of bromine and iodine compounds, alone and in presence of sulphur, gives further confirmation of the value of sulphur as an E.P. additive. The use of the method of pre-formation of films has indicated the general value of this technique in the elucidation of the mechanism of action of E.P. additives. The formation of addition complexes by halogen compounds and reactive sulphur compounds is of importance in the mode of action of the chlorine compounds at present in use as E.P. additives and also in the use of halogen compounds and sulphur or sulphur compounds together for E.P. lubrication.

ACKNOWLEDGMENT.

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LIQUID FUELS AND CHEMICAL PRODUCTS FROM PETROLEUM AND COAL.*

By Prof. F. H. GARNER, O.B.E., Ph.D., F.R.I.C. (Fellow).

IN air transport, only liquid fuels are used and in transport by land and sea, liquid fuels are being used to an ever-increasing extent. . The replacement of solid fuels for transport purposes is almost inevitable in view of the great advantages inherent in the ease of handling of a liquid, both in making provision for supplies at a given point and in the power unit itself. Use of pipelines, tankers, and even road tankers present many advantages in rapidity and ease of supply, but it is principally in the engine or power unit that the advantages of liquid over solid are greatest, particularly when relatively small units are required, as in road and rail transport. For road transport, liquid fuels are used in internal combustion engines, either spark ignition or compression ignition, and it is estimated that 75 per cent of merchant shipping use fuel oil to-day as compared with 4 per cent in 1914.

Solid fuels have their main industrial application in larger stationary units for power development where the additional equipment necessary for automatic control and efficient use of the fuel can be incorporated. An exception to this is space heating, both domestic and industrial, which constitute such a large proportion of the total fuel consumption that economy in heat production is of the greatest importance. It appears desirable for space heating to use primary raw fuels, such as coal or petroleum, rather than those obtained by the consumption of a substantial proportion of the fuels such as electricity, which latter fuels are preferably used as the "topping up" source of heat.

During the war intensive effort was concentrated on the development of gas producers for road transport, particularly in some countries in Europe, where the need was pressing owing to the fact that no gasoline was available. For example, road transport in Sweden used mainly gas producers during the war years, but at the present time there is an insignificant number in use, gas generators having been quickly discarded as soon as gasoline became available.

Road Transport in Sweden using Gas Generating Systems.

	Passenger cars.	Buses.	Trucks.	Total.
1944 . . .	34,716	3,531	34,416	72,663
1945 . . .	35,205	3,511	34,174	72,896
1946 . . .	196	16	118	330
1947 . . .	Possibly 150 total.			

* Opening paper presented to Section IX, Chemistry in Relation to Fuel, Power, and Transport, at the XIth International Congress of Pure and Applied Chemistry, London, July 18, 1947.

Compressed gaseous fuels have the same advantages as liquid fuels in ease of flow and control, but for transport purposes the extra weight of the cylinders has prevented the widespread use of gases.

It appears to be accepted that atomic energy plants for some years to come will be relatively large power units and it is difficult to see any possibility of atomic energy being used for either road or air transport until some new developments occur. When atomic, or rather nuclear, energy has been developed as a source of power it is possible that it will be used to produce liquid fuels especially suitable for spark or compression ignition engines (piston engines) or turbines from such raw materials as coal or petroleum.

LIQUID FUELS FOR POWER GENERATORS.

The use of liquid fuels in internal combustion engines is so well established that it is unlikely to be replaced for many decades.

For internal combustion engines with spark ignition which use volatile fuels, such as gasoline, the demand is for high octane fuels owing to the increased efficiency obtainable with high compression ratios; this led to the development of aviation fuels largely composed of synthesized hydrocarbons, for example, *iso*-octane and aromatic hydrocarbons such as cumene or butyl-benzene, with the addition of the anti-knock reagent, tetra-ethyl lead.

For internal combustion engines with compression ignition, where less volatile fuels of lower cost are mainly used, the demand is for readily ignitable fuels of high octane number, mainly paraffin hydrocarbons; such fuels have been obtained chiefly from suitable crude petroleums, although they have also been made by the Fischer-Tropsch process and partly by hydrogenation and solvent refining. Little industrial use has been made of knock-promoters to improve cetane number as none of similar efficacy as tetra-ethyl lead—for suppressing knock—has been discovered.

The compression ignition or diesel engine is having more and more extended use, up to 150 h.p. for road transport and from 350 h.p. for diesel shunting locomotives to 1500 to 2000 h.p. for main line trains in rail transport, and in a wide variety of sizes for fishing and marine transport from, say, fifty to many thousand h.p.

The principal external combustion engines or pistonless engines (gas turbines)—which will replace the normal spark ignition engine in air transport in the course of time—are apparently not so particular as other types of engines in their quality demands for the fuel. Principally kerosine is used at present, but for larger units for sea and land transport cheaper fuels will be necessary to compensate for the lower efficiency of the turbine as compared with the compression ignition engine. Thus residual fuel oil will be required or powdered coal as described in one of the papers in the present session.

LIQUID FUELS FOR HEAT GENERATION.

Brief reference should be made to the position of the more viscous liquid fuels as compared with solid fuels, in applications where the fuel is burnt

to generate heat rather than power directly. Liquid fuels (such as residual fuel oils) have an advantage over solid fuels in these processes in which on the one hand, a high radiant heat is necessary, or on the other, the comparative freedom from impurities, such as sulphur and ash, as, for example, in the manufacture of steel in open-hearth furnaces, and glass melting respectively. In these high-temperature processes, 1 ton of oil can do the work of 2 tons of coal, with an increase in output. It is, however, doubtful whether it is justifiable in Great Britain, when coal is available, to use imported fuel oil on industrial boiler plants, or even in steam raising in rail transport, as no corresponding thermal saving is obtained. However, by the use of fuel oil in diesel engines for rail transport as compared with steam engines, only from one-seventh to one-twelfth of the liquid fuel on a B.Th.U. basis is necessary for a given duty.

Hitherto the bulk of the liquid fuels have been derived from petroleum sources, although liquid hydrocarbons for commercial use from coal and shale antedate the use of petroleum. James Young with his associates Binney and Meldrum made kerosine from both coal and shale as early as 1852, before the discovery of the Drake Well in 1859. Germany obtained nearly the whole of her aviation fuel from the hydrogenation of brown bituminous coal; Fischer-Tropsch plants using water gas were developed somewhat later than the hydrogenation plants and the maximum output was only 15 per cent of the total liquid fuel production from coal.

Fischer-Tropsch Process.

For fuel production, the process is operated at atmospheric pressure using cobalt catalysts and H_2 : CO ratio 2 : 1, about 15 per cent of methane and ethane being produced. Raising the pressure to 10 atmospheres with slightly lower H_2 : CO ratio, gave less gas and a higher yield of the soft and hard wax. Whilst the diesel fuel from the Fischer-Tropsch process is of high cetane number, the gasoline has too low an octane number for direct use as motor fuel.

With cobalt catalyst, H_2 : CO 1.25 : 1, and recirculating residual gas, the olefin content of the middle fraction 200–320° C could be raised to 45 per cent. With sintered iron catalysts under suitable conditions, 70 per cent of olefin could be obtained in the gasoline fraction : again, with ruthenium catalyst, products containing about 60 per cent of a high m.p. wax could be obtained. Normally, methanol is obtained with zinc chromate catalyst from water gas, but by suitable modifications of the process, with an alkaliized iron catalyst, as much as 50 per cent alcohols in the boiling range 150 to 300° C could be obtained.

Thus by the Fischer-Tropsch process a wide range of olefins, alcohols, and paraffin waxes can be obtained, all potentially valuable sources of synthetic chemicals, and it appears that it is in this field, rather than fuels, that the opportunities of this process lie.

Whilst in Germany the Fischer-Tropsch process could not compete with hydrogenation as an economical process for making liquid fuels, the application of the fluid process developed for catalytic cracking of petroleum oils may alter the situation. The heat of reaction of the synthesis gas in the Fischer-Tropsch process is very great and the temperature has to be controlled to about 10° C. Elaborate cooling arrangements with an

enormous heat transfer area are necessary in the German equipment to maintain the required temperature control. The fluid process provides a method for simpler heat removal and also for maintaining the intimate contact between the relatively large volume of catalyst and the reacting gases for fuel production.

In the United States, where cheap natural gas and low-cost coals are available, plants have been erected recently to use the Fischer-Tropsch process with low-cost synthesis gas from these sources and from residual liquid fuels. One of the most recent is a joint investigation between coal and petroleum interests for the manufacture of gasoline, diesel fuel, and alcohols, together with gas to replace or supplement natural gas for industrial and domestic use.

Coal and Petroleum as Sources of Liquid Fuels.

Whilst there is no shortage at present of crude petroleum the costs of liquid products from coal and crude petroleum are getting nearer equality and the world's reserves of coal are much greater than those of petroleum. As regards petroleum, the United States produce about 60 per cent of the world total, but her reserves are only 34 per cent of the total, and her crude petroleum is being consumed at a rate of about 6 per cent per annum, whereas for the vast Middle East petroleum reserve the rate is probably much less than 1 per cent.

The main use of coal and petroleum is at present, and is likely to remain for a long time to come, mainly as a source of power. From petroleum about 40 per cent of gasoline is produced, 6 per cent of kerosine, 4 per cent lubricants, 20 per cent distillate fuel used for domestic heating, and about 10 per cent diesel fuel and 10 per cent of residual fuel, together with about 10 per cent of miscellaneous products such as asphalts. Approximately 10 per cent of the world's gasoline comes from natural gas and of the remaining 90 per cent, 40 per cent is that naturally present in crude petroleum and 50 per cent is obtained by cracking higher boiling fractions. Whereas cracked gasoline before the recent war was nearly all made by thermal cracking at high pressures, now only two-thirds is produced by this method—the remainder being obtained with the help of catalysts as in the Houdry, T.C.C., and fluid catalytic processes developed during the war.

In future there will be a considerable increase in the demand for diesel fuels which represent such an efficient source of power generation. In addition, there is expected to be a great increase in distillate fuels owing to the ease with which these low viscosity fuels can be used for domestic heating with automatic and easy control of temperatures. These increases in middle distillates together with demands for aeroturbine fuels can be partly effected by a conversion of residual fuels used at present primarily for power and heat generation and partly, if required, by less cracking for gasoline. There is at the present time a great shortage of middle distillates, and the late Lord Cadman in his presidential address to the Institute of Petroleum as far back as 1936, said: "*neither is it an impossible exaggeration to think that a time may emerge when the development of the compression ignition engine will render it desirable to convert a future excess of spirit into fuel for that type of engine. To do so would be a remarkable reversal of current*

procedure." He pointed out that at that time, allowing for the loss in yield on cracking, a mileage of nearly double could be obtained with gas oil as with the gasoline obtained from it by cracking. Nearly 90 per cent of petroleum and an even larger percentage of coal is used as fuel, and fuel is likely to remain the main use of all hydrocarbons. From petroleum, most of the synthetic products have been made from cracked gases (rather less than 1 per cent of the crude petroleum) utilizing hydrocarbon fractions especially suitable for such purposes.

NEWER SYNTHETIC CHEMICAL PRODUCTS.

Coal, petroleum, shale, and natural gas are all available as sources of synthetic chemicals particularly in view of the development of the Fischer-Tropsch and hydrogenation processes.

The chemical products made from hydrocarbon sources can be grouped into three types.

First, those separated or made without major alteration of the source material.

Secondly, products built up from one of the simpler molecules, as, for example, from C_1 to C_4 , methane to butane, the so-called chemical bricks which are normally obtained by cracking or destructive distillation of the natural product.

Thirdly, products derived from higher boiling products, that is from a group of hydrocarbons rather than the individual hydrocarbon used in the second method.

Products Directly from Coal and Petroleum.

Relatively little use has been made of coal as a raw material although the manufacture of base exchange reagents from coal may be considered as being in this category, and there are a number of pending developments in this field, such as the manufacture of benzene carboxylic acids. Ester-waxes from peat, which is the subject of a paper in this session, is a similar development.

In petroleum, oxygen, sulphur, and nitrogen compounds are present in small proportions which represent very large quantities from the point of view of the chemical industry. Naphthenic acids, mainly carboxylic acids from cyclopentane, are being increasingly made available from such crudes as Venezuelan, Mexican, and Trinidad for a wide variety of uses, as in emulsifiers, fungicides, paint driers, and extreme pressure lubricants. Phenols are extracted from cracked petroleum products to supplement those available from coal tar, where nitrogen compounds, principally quinoline bases, have not so far been extracted for commercial use. Similarly aromatic and other high carbon-hydrogen ratio hydrocarbons derived from lubricating oils by solvent refining in the form of extracts are being used for such purposes as rubber compounding and as semi-drying oils in the manufacture of putty, paints, printing inks, etc.

All these products are mixtures, often highly complex mixtures, but are characterized by some common feature such as the presence of a carboxylic group or a phenolic group or a very high carbon-hydrogen ratio.

Chemicals Synthesized from Simple Molecules.

The second type, made from simple molecules, gives less complex mixtures and may give individual chemical compounds, as for example 2:2:4-trimethylpentane, isooctane from butene, glycerol from propylene, or ethyl alcohol from ethylene in coal gas. The source materials are primarily the olefins, ethylene, propylene, and the butylenes, although the corresponding paraffins and dienes are also used, and the simpler aromatic hydrocarbons and phenols from coal tar.

In Germany, Reppe developed a new technique of handling acetylene and thus made it a convenient source of certain synthetic chemicals, particularly vinyl compounds. Carbide manufacture in Great Britain does not, however, seem a suitable source of hydrocarbons, since some 70 to 75 per cent of the fuel is wasted in producing the electricity required.

Whilst the earlier synthetic chemical industry founded by Perkin was largely based on aromatic hydrocarbons, discovered by Faraday in cracked products and later isolated from coal tar, more recently there has been a synthetic chemical industry which has been largely based on olefins from cracked petroleum. There have, however, been some interesting combinations of olefins and aromatics as of butadiene and styrene in synthetic rubber, of formaldehyde and phenol in plastics, and of aromatic and straight chain paraffins in detergents.

Recent estimates of the proportion of synthetic chemicals made in the United States from petroleum vary from about 25 to 50 per cent, depending on whether such hydrocarbons as isooctane and toluene are excluded or included in the term synthetic chemicals.

Certain synthetic products of wide industrial application—really key products—such as ethyl alcohol are being increasingly made from petroleum and some 40 per cent is estimated to have been made from this source in the U.S.A. in 1946 as against 60 per cent from molasses. The grade of alcohol produced is at least as pure as that from the fermentation process: as starting material, ethylene produced by vapour phase cracking of ethane and propane, is converted into sulphonic acids by absorption in sulphuric acid. This is then hydrolized to the alcohol. This source will be supplemented later on by ethyl alcohol from the Fischer-Tropsch process.

Methane, the main constituent of natural gas, is a source of formaldehyde and methyl alcohol and one gas well could supply the world demand for formaldehyde.

Ethane and ethylene are the sources of acetaldehyde, ethyl alcohol, and other ethyl compounds and of vinyl and vinylidene compounds together with the polymer poly-ethylene. Propylene was the source of the first synthetic chemical made from petroleum, namely, isopropyl alcohol, and from this compound acetone, acetic anhydride, and acetic acid are manufactured. By the chlorination of propylene, allyl chloride is obtained which is now to be developed as a source of glycerine and various allyl derivatives.

These and other chemical intermediates built up from the simpler hydrocarbon molecules and carbon monoxide are the bases on which the larger synthetic chemical industries such as plastics and synthetic fibres depend; the earlier dyestuffs industry and pharmaceutical chemicals were largely dependent on aromatic hydrocarbons derived from coal tar, but both coal

and petroleum are now available as a source material for aromatic hydrocarbon.

In the manufacture of isooctane from butane and butylenes, a range of manufacturing techniques of cracking, polymerization, isomerization, and alkylation were developed, which have been employed in a wider field, just as the fluid catalytic cracking process is now being considered in shale oil extraction, in the Fischer-Tropsch process, and in the oxidation of naphthalene to phthalic anhydride. The alkylation reaction originally described for the manufacture of 2 : 2 : 4-trimethylpentane from isobutene and butylenes by contact with sulphuric acid and later with other reagents, such as aluminium chloride, phosphoric acid, and hydrofluoric acid, was applied to the manufacture of cumene from benzene and propane-propylene mixture, and to tertiary propyl benzene (Victane) from benzene and butane-butylene mixtures.

Butadiene was manufactured by the cracking of butane in the presence of steam and then suddenly chilling the products to stop the reaction and minimize decomposition of the butadiene. Nearly half a million tons were made from petroleum for use in synthetic rubber in 1946 and this represented less than 1 per cent of the crude petroleum processed. Styrene, the other component in synthetic rubber, and also used for manufacture of polystyrene, was made from benzene and ethylene derived from cracked gases, the resulting ethyl benzene being steam cracked as in the manufacture of butadiene. Toluene was extracted from petroleum in large quantities, but much larger quantities were obtained by hydroforming of suitable stocks containing methylcyclohexane, dimethylcyclopentane, and heptane, which were dehydrogenated to give toluene. In the same way other aromatic hydrocarbons such as benzene and *ortho*- and *para*-xylenes were made.

Thus chemical compounds derived from hydrocarbon sources are available for the manufacture of nearly all the different types of plastics (except the first commercial plastic, cellulose nitrate) as even in cellulose acetate and the ethyl celluloses the acetic acid and ethyl chloride are now made from ethylene or ethane.

Of the synthetic fibres, nylon is a polyamide made from adipic acid derived from cyclohexane which is itself made from benzene from coal or petroleum.

Another synthetic fibre, terylene, is derived from terephthalic acid and glycol of which the former is made from *para*xylene and the latter from ethylene.

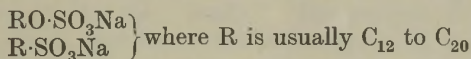
Vinyon, another new fibre, is made by copolymerization of vinyl chloride and acrylonitrile, both of which are ethylene derivatives.

Products from Mixed Hydrocarbon Fractions.

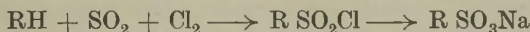
The third type uses fractions of a wider boiling range with a number of different hydrocarbons present, and thus a much more complex starting material. Examples are the manufacture (1) of fatty acids from paraffin wax; (2) of sodium sulphonates of hydrocarbons for detergents from olefin fractions from paraffin wax or from the Fischer-Tropsch process; and (3) of aldehydes by the OXO process from similar olefin fractions by reaction with water gas in the presence of cobalt catalysts.

1. *Fatty Acids.* In the manufacture of fatty acids by the oxidation of paraffin wax in the presence of potassium permanganate, conversion is allowed to proceed until about one-third of the theoretical yield is obtained, after which the fatty acids are extracted. Germany was estimated to have plant capacity in war-time of 80,000 tons per annum. From part of the fatty acids synthetic butter was produced by esterification with glycerol, and was said to have been largely reserved for submarine crews on account of its good keeping qualities.

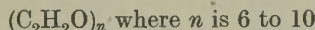
2. *Detergents.* These are normally made from mixtures of long chain molecules which may be hydrocarbons derived by the cracking of petroleum or paraffin wax, or from olefins derived from the Fischer-Tropsch process. Sulphonated detergents have the structure :



and are made by sulphonation of olefins or alcohols, although the Germans also developed other methods of sulphonation in the presence of ultra-violet rays or ordinary electric light as follows :



In Germany as much as 75,000 tons of synthetic detergents were made annually, largely from Fischer-Tropsch gas oil, but the detergents also included other products containing long chain ethylene oxide molecules



with or without a sulphonated group.

3. The OXO process gives aldehydes directly, but these may be readily converted into alcohols, carboxylic acids, soaps and esters.

Products containing Nitrogen, Sulphur, Fluorine, and Silicon.

So far reference has been made primarily to compounds containing carbon, hydrogen, and oxygen, but there have been important developments recently with compounds derived from hydrocarbon sources containing nitrogen, sulphur, fluorine, and silicon.

Nitroparaffins have good solvent properties and are a source of aliphatic amines.

Butane is dehydrogenated by reaction with sulphur to give first butylene, then butadiene, and, finally, ring formation to give thiophene. As by-products of this reaction, carbon disulphide and thiophene thiol are produced. Thiophene is, of course, of value as a solvent and in the manufacture of pharmaceuticals and dyestuffs.

The development of fluorine chemistry of hydrocarbons in war-time has been particularly marked in connexion with the utilization of atomic energy, and the whole of one issue of the *Industrial and Engineering Chemistry*, namely, that for March 1947, was devoted to the problem of the industrial scale development of fluorine and of fluoro-hydrocarbon processes.

The silicones based on the pioneer work of Kipping are now being used extensively in such diverse applications as heat resisting plastics, flat viscosity-temperature lubricating oils, and froth dispersers.

Thus hydrocarbon sources promise to be of increasing importance in the manufacture of synthetic chemicals and chemical products. So far the manufacture of synthetic chemicals has been largely from individual hydrocarbons mainly derived from decomposition products, such as tars and crude gases. Whilst the process of building up from small molecules will probably continue to be the main source of synthetic chemicals for hydrocarbon sources, it would appear that in the future there will be increasing use made of fractions of mixed composition as is the case with other natural starting materials, such as the celluloses, carbohydrates, or fatty acids.

SOLVENT EXTRACTION OF INDENE AND COUMARONE FROM COAL TAR LIGHT OILS.*

By A. W. GAUGER † and J. N. BRESTON.†

IN the commercial carbonization of coal for the production of gas and coke, ammonia, light oils, and tar are obtained as main by-products. The light oils, chiefly benzene, toluene, xylenes, and higher members of this aromatic series, are recovered by scrubbing the gases with light petroleum oil (wash oil) and subsequent recovery by distillation of the solution, and by distillation of the tar "crude." The portion of the light oil boiling above the xylenes and below 200° C is separated as the solvent naphtha fraction which has found widespread use as a general solvent. Certain resin-forming compounds found in the solvent naphtha fraction have received considerable attention. These are styrene, indene, and coumarone. Their polymers have found use in varnishes, rubber compounding, printers' inks, plasticizers, paper sizing, electrical insulation, substitute for chicle, etc.

The separation of indene and coumarone in pure form from the solvent naphtha fraction is difficult even by efficient fractional distillation. Indene is unstable and oxidizes easily in contact with air. Coumarone is fairly stable, but it occurs in the light oil along with numerous other compounds having nearly the same boiling point, so that it is extremely difficult to obtain pure coumarone by distillation.² It became apparent as early as 1890, when Kramer and Spilker^{4, 5} first isolated indene and coumarone from coal tar light oil, that for commercial purposes other methods of separation were necessary. Thus they experimented with and patented a process⁶ in which the indene and coumarone were precipitated out of the light oil as picrates and subsequently recovered by decomposition of the picrates with steam. However, their product was quite impure and the method of preparation proved expensive and hazardous. Spilker and Dombrowski⁷ in 1909 evolved a better procedure for the preparation via picrates, but the product still was impure. Lately investigation by Breston¹ has shown that the indene-coumarone concentrate obtained via picrates contains as much as 18 per cent of compounds other than indene or coumarone. He has also shown that efficient fractional distillation will separate pure indene from this concentrate, but pure coumarone may be obtained only by repeated distillations and then only in very small yield.

In 1909 Weissgerber⁹ prepared a sodium indene compound by reacting a light oil fraction with metallic sodium or sodamide. He also prepared a potassium indene compound by heating an indene fraction with solid KOH. Decomposition of these compounds with water produced indene.

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He patented a process¹⁰ using the latter method for preparing indene from the indene fraction (175° to 185° C) of tar oils. The expensive and risky nature of the process precluded its commercialization. Walters⁸ found it safer to use sodamide in preparing sodium indene, but it gave lower yields.

Separation of indene and coumarone as polymers from the indene-coumarone fraction of light oil later became the most common commercial method for their recovery. The method consists of thermally treating the fraction under controlled conditions with or without the use of catalysts, such as H_2SO_4 or metallic halides. After reaction the catalyst is removed, the unreacted oils distilled off, and the polymer oils recovered by steam distillation. However, these polymer oils are not pure and contain polymers of indene and other aromatics. The resins prepared from these oils have poor colour stability and their use in such products as varnishes has been limited.

In 1934³ a patent was granted on a process for the recovery of "practically pure" indene by fractional distillation and crystallization at -25° C. The term "practically pure" was not defined. Apparently coumarone was not recovered in this process since its freezing point is -28.9° C.²

A survey of the literature indicates that no attempt has been made to use selective solvent extraction for the separation of indene and coumarone from tar light oils. There is considerable literature on the separation of pitch from tar oils, separation of aromatic from non-aromatic hydrocarbons, and the solvent extraction of tar oil motor fuels, but so far the coal tar industry has not reported any specific use of solvent extraction for indene and coumarone. Considering the tremendous industrial use of solvent extraction especially by petroleum refiners and the great advances made in its fundamentals and practice, it is surprising that such limited use has been made of this tool by the coal tar oil refiners.

This paper is a report of preliminary investigations into the use of selective solvent extraction for separating indene and coumarone from coal tar light oils.

PREPARATION AND PROPERTIES OF INDENE AND COUMARONE.

The preparation and properties of the pure indene and coumarone use in this work have been outlined in detail in another paper.² The indene was prepared from an indene-coumarone fraction of light oil by precipita-

TABLE I
Properties of Indene and Coumarone.

	Indene.	Coumarone.
Boiling point at 760 mm.	182.57 ± 0.05° C.	171.38 ± 0.05° C.
" " 100 "	114.5 ± 0.1° C.	105.2 ± 0.1° C.
" " 10 "	60.7° C.	53.2° C.
Density, d_4^{20}	0.9960	1.0948
Refractive index, n_D^{20}	1.5766	1.5663
Freezing point	-1.64° C.	-28.9° C.

tion as picrates, decomposition and distillation by steam, and two vacuum fractional distillations. The coumarone was prepared by the decarboxylation of coumarilic acid which was synthesized from coumarin. The crude coumarone oil from the decarboxylation was fractionated to give pure coumarone. Some of the properties of the indene and coumarone are found in Table I.

SOLUBILITY TESTS.

Solubility tests on indene and coumarone showed them to be completely miscible with most common solvents, such as alcohols, ethers, ketones, light oils, naphthas, petroleum oils and naphthas, pyridine, carbon disulphide, turpentine, carbon tetrachloride, chloroform, etc. In fact they turned out to be very good solvents themselves. Further tests showed them to have partial or total solubilities in such compounds as glycols, amines, poly-amines, ethanol-amines, and acetone-water mixtures.

In the search for a suitable solvent for the selective extraction of indene and coumarone from light oil it was necessary to find one which would be specific for these compounds or one which would have a greater solvent power for indene and coumarone than for the remainder of the constituents of the light oil. This remainder of the light oil, although predominantly aromatic, would be essentially non-olefinic and could be called the "diluent" from which indene and coumarone are to be extracted. Therefore in the analysis of solvents their solvent power for the "diluent" had to be determined along with their solvent power for indene and coumarone. A commercial grade of refined solvent naphtha (B.P. 145° to 180° C) is a good example of such a "diluent." The indene and coumarone and other "gum formers" have been removed by acid treatment. Such material was used as the "diluent" in the solubility tests.

Due to the limited supply of pure indene and coumarone the tests were performed on a small scale—2 to 5 ml at a time. The solvents used were pure or of a good technical grade. Wherever possible the composition of the layers was determined by volumetric and refractometric means, and in other cases by a modified bromine addition test.¹ Inasmuch as most of the solvents tried were exceedingly water soluble, such as the glycols and amines, analysis was facilitated by extracting these solvents with water in Babcock milk or cream test bottles. Centrifuging easily separated the oil from the water solvent solution.

In Table II are found the results of tests on the solubility of indene, coumarone, and refined solvent naphtha in the various solvents tried—as well as the solubility of the solvents themselves in these compounds. No one solvent was found which was 100 per cent specific for indene and coumarone. It may be possible to find one, but this seems quite improbable. On the other hand, certain glycols and amines were found which showed a greater solvent power for indene and coumarone than for the "diluent" refined naphtha. These have immediate possibilities as selective solvents for the extraction of indene and coumarone. Other solvents, such as polyglycols and some poly-amines, are completely miscible with indene and coumarone, but only partly miscible with the refined naphtha. These may be used for selective solvents, but their efficiency would be limited. Acetone-water mixtures and alcohol-water mixtures appear as likely selec-

tive solvents. Solvents which may contain traces of acids or which easily hydrolyze into acids were avoided since acids are notorious catalyzers of the polymerization of indene and coumarone.

SOLVENT EXTRACTION OF INDENE AND COUMARONE WITH ETHYLENE GLYCOL SOLVENT.

Having found a number of solvents which have a preferential solvent power for indene and coumarone, the next step was to apply one to solutions of indene and/or coumarone in refined naphtha. Ethylene glycol was selected as the test solvent in this experiment inasmuch as its solvent characteristics as shown in Table II appear to make it a most practical

TABLE II.

Solubility of Indene, Coumarone, and Refined Naphtha in Various Solvents and Solubility of the Solvents in these Compounds.

Weight per cent.

Solvent.	Indene.		Coumarone.		Refined naphtha.	
	Indene in solvent, per cent.	Solvent in indene, per cent.	Coumarone in solvent, per cent.	Solvent in coumarone, per cent.	Naphtha in solvent, per cent.	Solvent in naphtha, per cent.
Ethylene glycol	3.6	1.3	8.0	7.3	1.6	1.3
Diethylene glycol	10 (est)	3 (est)	25 (est)	10 (est)	5 (est)	2 (est)
Triethylene glycol	40	11.5	completely miscible	"	8	5
Tetraethylene glycol	completely miscible	"	"	"	16	2
Hexaethylene glycol	"	"	"	"	18	1.5
Nonaethylene glycol	"	"	"	"	22	1
Propylene glycol	10	<1	22	<1	6	5
Dipropylene glycol	completely miscible	"	completely miscible	"	completely miscible	"
Ethylenediamine	1.6	3.6	4.1	5	<1	1.6
Propylenediamine	completely miscible	"	completely miscible	"	completely miscible	"
Diethylenetriamine	"	"	"	"	32	<2
Triethylenetetramine	"	"	"	"	completely miscible	"
Tetraethylenepentamine	"	"	"	"	"	"
Monoethanolamine	9	<1	21	1	3.0	<5
Diethanolamine	9	<1	25	<1	3.2	<5
Triethanolamine	14	<1	41	—	3.8	<5
Ethylmonoethanolamine	completely miscible	"	completely miscible	"	completely miscible	"
Ethylmethanolamine	"	"	"	"	"	"
Diethylaminoethanol	"	"	"	"	"	"
Furfural	"	"	"	"	"	"
Furfuryl alcohol	"	"	"	"	"	"
Methyl acetate	"	"	"	"	"	"
Nitromethane	"	"	"	"	"	"
Pentachlorethane	"	"	"	"	"	"
Triglycoldichloride	"	"	"	"	"	"

one because it has a low solvent power for the compounds involved. This would enable the use of a high ratio of solvent to naphtha solution (of indene and/or coumarone) giving greater extracting efficiency.

Prepared mixtures of indene or coumarone in refined solvent naphtha were batch extracted at room temperature with ethylene glycol. The extracting consisted of thoroughly shaking the materials in a specially prepared graduated cylinder until the phase equilibrium was established. If the layers did not separate readily on standing, centrifuging was employed.

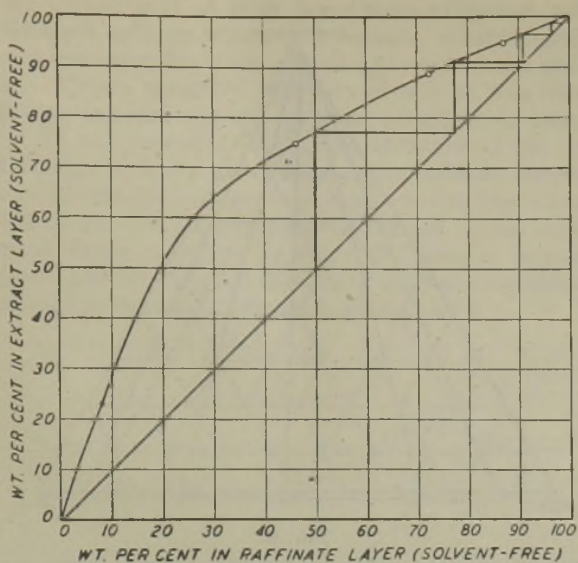


FIG. 1.

EQUILIBRIUM DISTRIBUTION OF INDENE BETWEEN EXTRACT AND RAFFINATE LAYERS FOR THE SYSTEM INDENE-NAPHTHA-ETHYLENE GLYCOL AT 30° C.

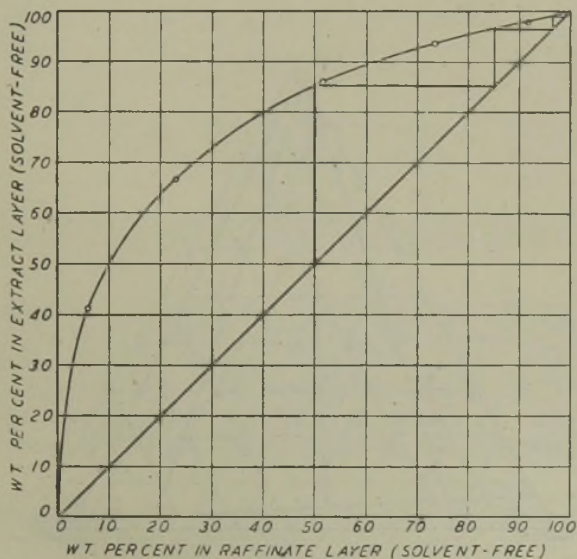


FIG. 2.

EQUILIBRIUM DISTRIBUTION OF COUMARONE BETWEEN EXTRACT AND RAFFINATE LAYERS FOR THE SYSTEM COUMARONE-NAPHTHA-ETHYLENE GLYCOL AT 30° C.

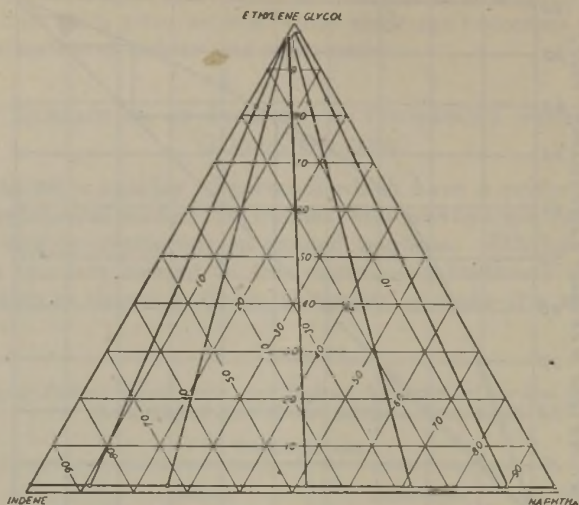


FIG. 3.

TRIANGULAR PHASE DIAGRAM FOR THE SYSTEM INDENE-NAPHTHA-ETHYLENE GLYCOL AT 30° C. WEIGHT PER CENT.

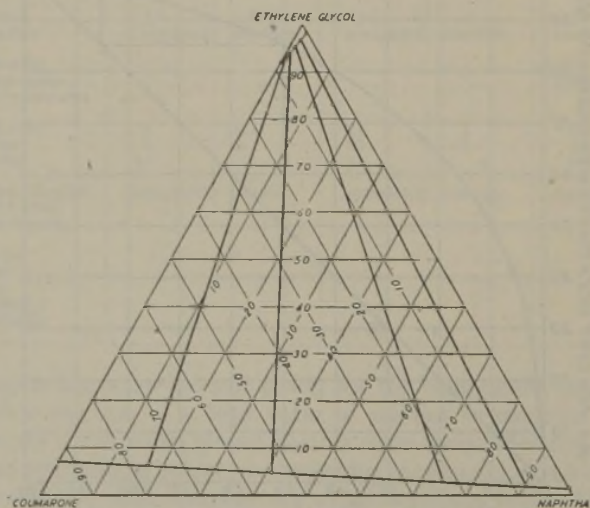


FIG. 4.

TRIANGULAR PHASE DIAGRAM FOR THE SYSTEM COUMARONE-NAPHTHA-ETHYLENE GLYCOL AT 30° C. WEIGHT PER CENT.

Then measured quantities of each layer were extracted with water in calibrated Babcock milk or cream test bottles. Centrifuging broke any stubborn emulsions, and the volume of oil was read on the graduated neck of the bottle. Then a measured quantity of this oil was titrated by the bromine addition method and the per cent of indene or coumarone thus determined. By this procedure data were obtained on the concentration of indene or coumarone in the extract and in the raffinate layers. The data were then used to plot the x - y curves as illustrated in Figs 1 and 2. Corresponding data giving the total composition of the layers were plotted on triangular co-ordinate paper to produce the ternary diagrams for the systems indene-naphtha-ethylene glycol and coumarone-naphtha-ethylene glycol. These diagrams are illustrated in Figs 3 and 4.

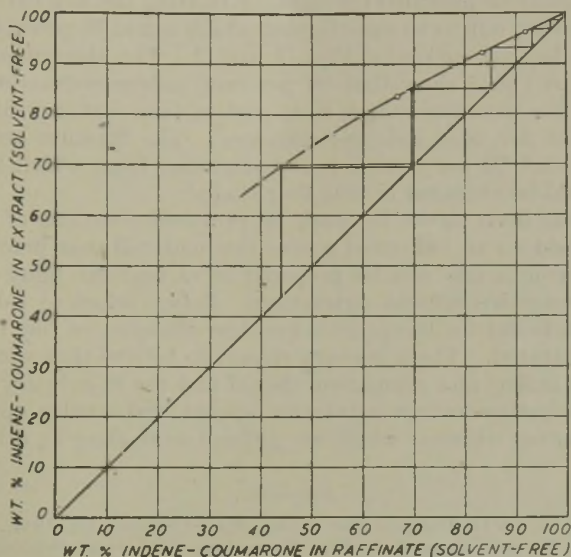


FIG. 5.

EQUILIBRIUM DISTRIBUTION OF INDENE-COUMARONE BETWEEN EXTRACT AND RAFFINATE LAYERS FOR THE EXTRACTION OF A BENZOL STILL RESIDUE FRACTION (160-200° c.) WITH ETHYLENE GLYCOL.

The x - y diagrams of Figs. 1 and 2 indicate that ethylene glycol is an efficient selective solvent for the extraction of indene and coumarone from refined naphtha. Theoretical stages stepped off on the diagrams show that four stages will extract 99 per cent indene from a 50 per cent solution in the refined solvent naphtha, and only three stages are necessary to extract 99 per cent coumarone from a 50 per cent solution in the naphtha.

SOLVENT EXTRACTION OF INDENE AND COUMARONE FROM A FRACTION OF UNWASHED BENZOL STILL RESIDUE.

Having demonstrated that indene and coumarone could be extracted from synthetic mixtures in refined solvent naphtha, it remained to be deter-

mined if these compounds could be extracted from an industrial coal tar light oil fraction in which they occur. One such industrial material is the unwashed benzol still residue of a by-product coke oven light oil. A fraction of benzol still residue boiling between 160° and 200° C was extracted with ethylene glycol according to the method described in the preceding section. However, in this case, the first extract was used as the starting material for the second extraction, etc. The total indene-coumarone content of the solvent-free extract and raffinate layers was determined by the method of bromine addition, and in the calculations the assumption was made that the ratio of indene to coumarone remained at about ten to one. No doubt the ratio changes, but the deviation would not cause more than a slight error in the calculated indene-coumarone content.

Three extractions provided the data for plotting the x - y curve in Fig. 5. The curve turned out to be exactly that which would be predicted from an analysis of the x - y curves of Figs. 1 and 2. The theoretical stages as stepped off in Fig. 5 show that 99 per cent indene-coumarone could be obtained in less than five stages from such a benzol still residue fraction containing 50 per cent indene-coumarone. The fraction actually used contained about 70 per cent indene-coumarone from which 99 per cent material could be obtained in only four stages.

Thus, it has been shown by work on prepared solutions of indene and coumarone and on an industrial source raw material that practically pure indene and coumarone can be prepared from coal tar light oils by the method of selective solvent extraction. A few selective solvents have already been found for the process and the efficiency of one of them has been demonstrated. There is every reason to believe that such a method of preparing indene and coumarone should find use in industry. Also, the process of selective solvent extraction should find similar application to other coal tar constituents which are difficult to recover by other means.

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OBITUARY.

ALFRED REGINALD CODE.

It is with regret that we record the death on September 10, 1947, at Cleveland, Ohio, of Alfred Reginald Code. Born in Melbourne, Australia, in 1901, he acted as assistant designing engineer to Crankless Engines Ltd. from 1922 to 1926 and then as chief draftsman and designing engineer until 1929.

In 1929 he entered the service of the Vacuum Oil Co. Pty. Ltd. as automotive engineer for New South Wales. In 1931 he was appointed chief engineer of the Automotive Engineering Division for Australia, New Zealand, and the Pacific Islands.

In July 1941 he was invited by the Director-General of Munitions Production, on behalf of the Commonwealth Government, to become Controller (later Director) of Armoured Fighting Vehicles, his task being to create and direct an organization to design and produce all types of such vehicles.

When the production of armoured fighting vehicles ceased in Australia in 1943, A. R. Code was appointed to the British Ministry of Supply as Deputy Director-General (Engineering) of Armoured Fighting Vehicles (and subsequently Director of Fighting Vehicles Development (Engineering)), a position which he held until the end of the war.

As an author he had many publications to his credit, these ranging from technical articles in scientific journals to more general contributions in the trade and daily press. He also contributed a number of papers to the Australian Institution of Automotive Engineers and similar bodies.

Alfred Reginald Code was elected a Member of the Institute in 1935 and transferred to Fellowship in 1939. He was also a member of numerous other societies connected with mechanical and automotive engineering and, in particular, was vice-president (1935-36) of the Institution of Automobile Engineers (Australia), its president (1936-38), and was appointed corresponding member for the United Kingdom and the U.S.A. when he came to London. By his early demise at the age of 46 the automobile industry is deprived of many years service from one fully qualified to give valued advice on design and engineering problems, and the petroleum industry loses one who was fully conversant with lubrication in relation to automobiles.

CHARLES ERIK CAPITO.

WE regret to announce the death on September 21, 1947, of C. E. Capito, who was first elected to membership of Institute of Petroleum in 1915.

He received his technical training at the City and Guilds Technical College and, after a period of service in the Assam oilfields, joined the Anglo-Iranian Oil Company in 1911. He became assistant fields manager

during the first world war, and in 1920 was appointed fields manager, Northern Area. In September 1923 he was transferred to the Southern Area where he remained until leaving the Company in 1928.

In the course of his service Mr. Capito opened many of the company's early test areas, some of which have now become producing fields; among these are White Oil Springs, Gach Saran, Agha Jari and Pazanun. He was also in charge of Naft Khaneh when oil was discovered in that area.

On leaving the Anglo-Iranian Oil Company he was appointed petroleum technologist to the Government of Trinidad, but after serving in that capacity for five years he suffered a very serious illness which left him with acute heart trouble and for some years he was an invalid.

In 1911 Mr. Capito was elected an Associate Member of the Institution of Civil Engineers and became a full Member in 1923.

He received the O.B.E. in the King's Birthday Honours in 1920.

As a Fellow of the Zoological Society he contributed many specimens of birds from Southern Persia to the Zoological Gardens and made a collection of bird skins from the same region, which are now in the Natural History Museum at South Kensington.

Mr. Capito leaves a wife and two children, to whom his many friends extend sincere sympathy.

WILLIAM HERBERT GODDARD.

MAJOR W. H. GODDARD, who recently passed away at the age of 73, was probably best known for his pioneer work in connexion with the development of the compression-ignition engine in Great Britain. He was responsible for the introduction of the first Mercedes-Benz oil-engined chassis into Britain and was subsequently associated with the use of this type of engine by several municipal transport undertakings. From 1931 he was directly concerned with road transport development connected with the Gardner engine.

He had been a member of the Institute since 1919 and contributed two papers on the subject of the diesel engine and road transport to the *Journal* in 1930 and 1933.

JAMES SMITH.

JAMES SMITH, who died recently in his 68th year, was well-known in Liverpool, where he had practised as an analytical and consulting chemist for many years. He was particularly interested in the analysis and examination of petroleum products and in the detection of dangerous gases in tank steamers. He was also joint patentee with G. Watson Gray of apparatus for the measurement of free water in dark oils.

He joined the Institute as a Member in 1922 and was transferred to Fellowship in 1939.