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PISTON DEPOSITS, RING STICKING, VARNISHING  
AND RING CLOGGING \*

By W. A. GRUSE and C. J. LIVINGSTONE.

## GENERAL PRINCIPLES.

THE two basic chemical changes in lubricating oils which underlie the formation of engine deposits are :—

(a) The thermal coking of the hydrocarbons under essentially non-oxidizing conditions.

This is what occurs in the familiar carbon-residue test. Two general influences govern the amount of residue left behind by coking. One is the molecular weight of the hydrocarbons, indicated roughly by the boiling point or the viscosity at some elevated temperature, such as 210° F. As molecular weight (or boiling point or viscosity) increases in any one family of oils, the carbon residue increases. The other influence is the chemical make-up. In a comparison of several oils of about the same molecular weight, the amount of carbonaceous residue on coking increases with the proportion of ring groups, particularly aromatics, present in the oil molecules.

(b) The oxidation of the hydrocarbons.

This is the change involved in the Sligh, Indiana, Underwood, and British Air Ministry tests.†

The mechanism of oil oxidation is not well understood, but in general there are two basic reactions which occur. If an oil molecule is paraffinic in nature, the oxidation products will at first be acids resembling the ordinary soap acids; in engine operation these may combine with metals present to form soaps. If the conditions are such that acids of low molecular weight are obtained, combination with metals will occur more readily than if the molecules are large. Ordinarily, the higher the oxidation temperature and the longer-continued the oxidation, the smaller will be the acid molecules produced.

On the other hand, if an aromatic or partly aromatic molecule is oxidized, the oxidation products, while somewhat acid, will fall predominantly in the class of resins, and as the oxidation proceeds, the products resemble more nearly ordinary asphalt, and are known as asphaltenes. These oxidized resins and asphaltenes are much more unstable on heating than are the oils from which they have been formed. Therefore they decompose

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\* Paper received 15th June, 1940.

† Sligh, *Proc. A.S.T.M.*, 1927, 27, Part I, p. 461.

Indiana : T. H. Rogers and B. H. Shoemaker, *Indust. Engng Chem., Anal. Ed.*, 15th Nov., 1934, 6, No. 6, pp. 419-440.

Underwood : H. C. Mougey, Preprint S.A.E. World Automotive Congress, New York Meeting, 23rd May, 1939.

British Air Ministry : Garner, Keeloy, and Taylor, *World Petroleum Congress, London (1933) Proceedings*, Vol. II, p. 448.

easily on further heating, yielding products of still higher carbon content and more solid consistency.

One fact of real significance about all these oxidation products is that as their molecular weight increases, they become more insoluble in all kinds of oils. This applies particularly to the soaps formed by oxidation of paraffinic oils, and to the resins and asphaltenes from aromatic and semi-aromatic oils. It applies all the more to the products of thermal cracking of the oxidized compounds.

Another significant fact depends on the difference in solvent power for oxidation products (particularly resins and asphaltenes) shown by different kinds of oils. The paraffinic oils are poor solvents, the aromatic relatively good solvents, and the semi-aromatic fall between.

Three physical changes which can and do occur in engine operation are important to the forming of engine deposits :—

(a) The evaporation, at moderate engine temperatures, of the lower-boiling (SAE 10 and 20) oils when they carry oxidation products in solution. While these oils boil normally under atmospheric pressure in the range 650–950° F., it should not be forgotten that at several locations in an engine they are spread in thin films and are exposed to the passage of blow-by gases. Under these conditions the ordinary vapour-pressure characteristics may cease to apply, so that evaporation will occur more readily. When such evaporation does occur, any dissolved oxidation products will be left behind on the evaporating surface, just as dissolved shellac is left behind when the solvent alcohol evaporates.

(b) The precipitation of products which have become insoluble because they have increased in concentration beyond the solubility limits, or because they have changed in chemical constitution. The first applies to the gradual accumulation of soaps, resins, and asphaltenes in oils undergoing crank-case oxidation. The concentration will increase until a limit is passed and a precipitate appears, usually as an asphaltic mud. As suggested, a paraffinic oil will tolerate much less dissolved material of this sort than will an aromatic oil. The second is exemplified by the separation from an oxidized oil, on heating, of decomposition products formed from oxidized compounds which were soluble until heated. With aromatic oils this separated product is likely to be first a sticky tar which becomes solid when cooled. It decomposes on further heating to a friable semi-solid which will not melt.

(c) The formation of emulsions of oil, usually contaminated with water, the emulsion stabilized by finely divided solids. The importance of these emulsions as such is familiar, but it is not so generally recognized that they may be dried in place, leaving voluminous granular deposits.

#### RING STICKING.

The cause of this phenomenon remains obscured in a cloud of controversy. So far as any influence which the nature of the oil may have, opinion, based on both published\* and unpublished information, is divided into

\* Fairlie, *Oil & Gas J.*, 1936, 34, No. 44, p. 114.

Larson, Ainsley, and Fairley, *ibid.*, 1936, 34, No. 39, p. 24.

Rosen, *J. Soc. aut. Engrs.*, 1937, 40, 165.

two camps. One adheres to the belief that ring-sticking tendency increases with the ease of oxidation of the oil (as indicated by laboratory oxidation tests), whilst the other believes that a volatile oil is best, ease of oxidation being relatively unimportant. The outstanding feature of the situation seems to be a large mass of contradictory experimental data. We believe this to be due chiefly to the fact that experimenters are using different types of engines under different operating conditions and that the very important mechanical details are being controlled to different extents. Each of the two opinions is undoubtedly sound, depending on the conditions under which it was deduced. In 1937\* we pointed out that either type of oil is likely to cause or not to cause ring sticking, depending on the conditions. The chemical fundamentals to be controlled are probably:—

- Ring-belt temperature.
- Rate of oil consumption.
- Extent of oil oxidation.

A discussion of these follows, but it seems desirable to comment first on the importance of mechanical conditions and details.

#### *Mechanical Influences on Ring Sticking.*

Among these are:—

- Ring-side clearance.
- Uniformity of ring-side clearance.
- Condition of cylinder wall surface, including ring conformation against cylinder wall.
- Material, design and reproducibility of pistons.

Since these variables must be controlled in test runs, they are factors which will influence the prevalence of ring-sticking in service.†

#### *Ring-side Clearance.*

The importance of this variable is obvious, and was pointed out by the authors in the 1937 paper just mentioned. In a supercharged test engine under otherwise rigidly controlled conditions, at an arbitrary wall temperature of 345° F. at the top of the cylinder barrel, and a ring-side clearance of 0.002 in. (to an accuracy of about 30 per cent.), ring sticking occurred in a given time period with all kinds of oils. When the side clearance was increased to 0.003 in., it was possible to recognize, in the same time period, variations in the performance of different types of oils. With continued running, a certain amount of normal wear is to be anticipated, so that side clearance will increase. We agree with the belief that much trouble can be avoided in service by increasing side clearance, but it should be remembered that with long-time running a wide clearance may increase to the point where harmful fluttering or surging may occur.

\* "A.S.T.M. Symposium on Lubricants," 1937, p. 13.

† Since this paper was presented, the importance of variable distortion of pistons when heated has been pointed out to us by A. L. Heintze and C. G. A. Rosen.

*Uniformity of Side Clearance.*

Uniform side clearance around the piston is obviously important. In order to avoid the normal increase in side clearance observed with aluminum pistons, we have done much of our work with cast iron. In one case we noted a gradual increase in sticking tendency of the top ring, when conditions were apparently unchanged from one test run to another; this was traced to an increase (by wear of the top land) in side clearance at one point in the circumference amounting to about 0.0022 in., compared with 0.0005 in. at a point opposite. A plot of the measurements around the groove is given in the accompanying Fig. 1. An examination of the diagram shows that opposite the exhaust valve the ring could not seat against the land. A path was thus open for hot blow-by gases to pass behind the ring and to decompose, into an adhesive cement, whatever oil products were there. This effect persisted even when cylinder wall temperature was lowered 100° F.

*Condition of Cylinder Wall Surface.*

At one point we encountered a very puzzling sequence of results. These are represented in the following tabulation. All conditions were rigidly controlled, sticking being induced by supercharging and a reproduced high wall temperature. The two oils used were of the same type, highly refined paraffinic. A new top ring was used in each run, the lower rings being retained to keep oil consumption the same.

Oil.	Oil consumption.	Sticking observed.
S.A.E. 40 . . . . .	10 gm./hr.	Top ring stuck; others free.
	This run repeated several times in succession with identical results.	
S.A.E. 20 . . . . .	9 gm./hr.	Top ring stuck; others free.
S.A.E. 20 . . . . .	39 gm./hr.	Top ring free; second ring stuck.
	Repeated several times with identical results.	
	(Run-in period, light load, on set of Ferrox rings; Ferrox rings then removed.)	
S.A.E. 20 . . . . .	19 gm./hr.	Top ring stuck.
S.A.E. 20 . . . . .	40 gm./hr.	Top ring free; second ring stuck.
S.A.E. 40 . . . . .	46 gm./hr.	Top ring free; second ring stuck.
S.A.E. 40 . . . . .	39 gm./hr.	Top ring stuck; second ring stuck.
S.A.E. 40 . . . . .	10 gm./hr.	Top ring stuck; others free.

The explanation of this sequence, as we worked it out, was as follows: the S.A.E. 40 oil formed a satisfactory lubricating film and left the cylinder wall in good condition. The oil consumption was low and the top ring stuck. The first run with S.A.E. 20 found the wall in good condition, and this lasted for the period of the test; oil consumption remained low. However, the viscosity of the S.A.E. 20 was not sufficient to maintain good lubrication very long at the prevailing wall temperature, and the second run with the 20 oil was sufficient to scuff the cylinder walls; oil consumption then went up sharply. This condition continued during repeated runs with the S.A.E. 20 until the wall was smoothed down by a low-temperature run with Ferrox rings. This surface lasted through one run with the S.A.E.

20 oil, after which it roughed up again. At this point a test run with S.A.E. 40 oil effected the same change as had been effected in a shorter time by the Ferro rings; however, during the polishing up the oil consumption was high. Once established, the surface maintained itself with continued use of S.A.E. 40 oil, and the test results were the same as in the first runs on S.A.E. 40.

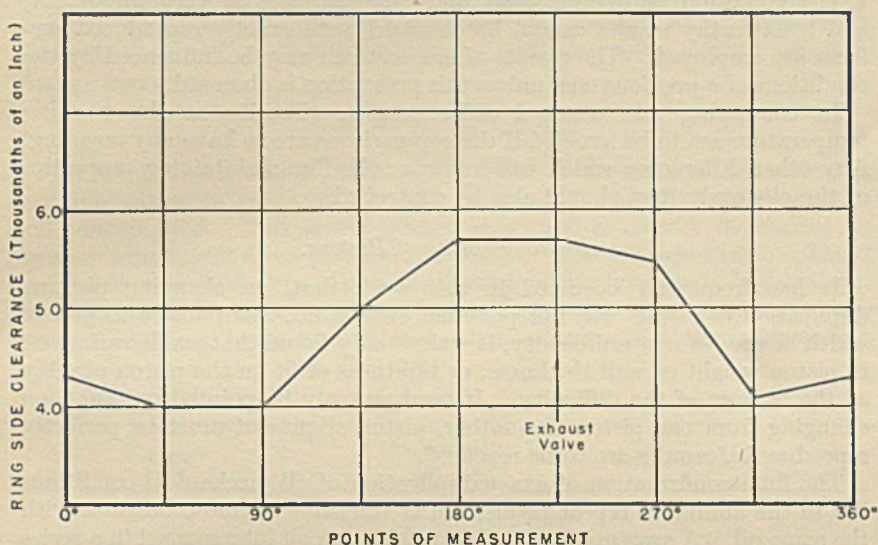


Fig. 1.

VARIATIONS IN RING SIDE CLEARANCE AFTER 195 HOURS OF RUNNING TIME. NORMAL CLEARANCE—3.5 THOUSANDTHS.

In order to confirm this explanation a second short series was made under the same conditions and with the same oils, except that the cylinder wall surface was observed by use of a profilometer.\*

The results are tabulated as follows:—

	Oil consumption.	Sticking observed.	Wall condition (average roughness, micro inches).
Control run—S.A.E. 40	12 gm./hr.	Top stuck; others free	—
No rougher spots anywhere	—	{ Top of ring travel	3
		{ Bottom of ring travel	8
Test run—S.A.E. 20 (A)	13 gm./hr.	Top free; second tacked	—
Repeat (B)	10 gm./hr.	Top stuck; others free	—
Repeat (C)	30 gm./hr.	Top tacked; second stuck	—
		{ Top of ring travel	8
		{ Bottom of ring travel	13
		Spot 1.5 in. below top of ring travel, 0.75 in. in diam., under exhaust valve	20-30

\* By courtesy of P. G. Exline, Gulf Research and Development Co.

Runs A and B are considered to be essentially duplicates, during which the scuffing had not advanced very far. Run C represents the incipient scuffing under discussion; continuation of this process would have ruined the cylinder wall.

The practical deductions from this series of experiments include the following points.

The condition of cylinder-wall and ring surfaces is very important, and trustworthy results cannot be obtained until exactly reproduced surfaces are employed. The results of one test run may be influenced by the conditions of a previous one, unless this precaution is observed.

In comparing oils, marked differences in viscosity at the working temperature are to be avoided if the comparisons are to have any meaning. Any other differences which will influence the film-maintaining properties of the oils under test should also be controlled.

#### *Reproducibility of Pistons.*

It has frequently occurred in this work that, on changing pistons, duplication of results was not possible. When not attributable to groove width or groove non-uniformity, it was usually found that small variations in piston weight or wall thickness, or tightness of fit on the piston pin, lay at the bottom of the difficulty. It need scarcely be pointed out that, on changing from one piston to another, piston alignment must be perfectly reproduced if results are to be repeated.

The final confirmation of exact duplication of all mechanical conditions lies in the ability to repeat results under the same engine conditions with the same oil. A system of control runs with one oil interspersed in a series of test runs is a real necessity. Rigid control of mechanical conditions is very difficult to attain, and an unbroken series of consistent results is scarcely to be expected.

#### *Chemical Influences on Ring-sticking.*

##### *Ring-belt Temperature.*

The influence of piston temperature in the ring belt has been discussed fully by Rosen.\* It has been possible in our present work to confirm the general correctness of Rosen's conclusions when piston temperature was varied only by changing wall temperature, engine output remaining constant. With a given paraffinic oil and a definite set of test conditions, the following sequence was obtained:—

Relative wall temperature, ° F.	
330	Deposits formed on piston land above top ring, and behind top ring; ring itself well lubricated and wet with oil. All lower rings clear of deposit.
345	Top ring stuck tight; second ring wet with oil.
360	Top ring and groove dry and clean; not lubricated; all oil was burning off. Deposit building up on land above second ring. Lower rings wet with oil.

\* *J. Soc. aut. Engrs.*, 1937, 40, 165.



It appears from these results that a particular optimum of temperature was located at which ring-sticking occurred most readily. Below this temperature sufficient liquid oil passed through the top groove to prevent accumulation of any serious amount of deposit. The piston below this point was cool enough to avoid deposition. Above this optimum temperature oil reaching the top groove was apparently burned away, so that no deposit accumulated. Just below this point on the piston the temperature was apparently right to permit the baking out of a deposit, which accordingly formed there. This last phenomenon has been observed in aircraft-engine operation.

#### *Rate of Oil Consumption.*

From our experience in this study we have been forced to conclude that no duplication in ring-sticking work is possible without close control of oil consumption. This is not always easy, and is usually dependent on proper adjustment of mechanical conditions. The following table is based on test runs in which type of oil and oil consumption were the only variables; all other conditions were closely controlled. The results illustrate the variations likely to be encountered when oil consumption is allowed to change.

Oil.	Consumption, gm./hr.	Sticking observed.
Low Oil Consumption.		
S.A.E. 30, solvent-refined naphthenic	15.3	All rings free.
	19.3	Top ring tacky but free; other rings free.
S.A.E. 40, paraffinic	16.8	Top stuck; others free.
	16.2	Top stuck; others free.
	11.2	Top stuck; others free.
High Oil Consumption.		
S.A.E. 30, solvent-refined naphthenic	36.8	Top stuck; second stuck.
	100.0	Top stuck; second tacky.
S.A.E. 40, paraffinic	39.6	All rings free.
	28.0	All rings free.

It will be observed that when oil consumption was low, the naphthenic oil left the rings free, whilst the paraffinic oil produced sticking. When oil consumption, on the other hand, was high, the reverse was encountered: the naphthenic oil stuck the rings and the paraffinic left them free.

The explanation of these differences is believed to lie in the variation in behaviour of the two oils. At a low rate of flow to the ring grooves the more volatile naphthenic oil apparently vaporized away rapidly enough and cleanly enough so that no appreciable residue of an adhesive nature was left on the rings; the less volatile paraffinic oil, however, at the prevailing temperature, left behind a sticky residuum which accumulated (was probably also oxidized) and finally bound the rings. When the oil flow past

the rings was approximately doubled, however, the residue from the paraffinic oil was kept diluted, so that it flowed up rapidly, and thus never had an opportunity of attaining a firmly adhesive condition. The naphthenic oil, by contrast, at a high rate of flow, evaporated only partly; the residue in the groove evidently then oxidized to a binding cement. This set of phenomena probably represents one of the underlying reasons for the prevailing differences of opinion as to the relative merits of paraffinic and naphthenic oils in reference to ring-sticking. The proponents of naphthenic oils are probably working with engines characterized by low oil consumption as related to piston temperature and output, whilst the proponents of paraffinic oils are perhaps concerned with engines which use more oil in proportion to piston temperature. This is discussed below.

#### *Extent of Oil Oxidation.*

The significance of oil oxidation in the ring-sticking picture is very difficult to evaluate. Oxidation in the ring grooves has been suggested as involved in the explanation just given as to why change in oil consumption affects the results from different type oils in different ways. There is much evidence for the belief that accumulation of oxidation products in crankcase oil will in many cases accelerate ring-sticking, but this probably gives too simple a view of the situation; facts are not yet available for a complete discussion.

Earlier in the paper it was pointed out that two schools of thought existed with regard to the importance of oxidation tendencies of oils. These seem to be based on real experience to the effect that in some cases clean burning-off in laboratory tests will select oils which do not stick rings, whilst in other cases resistance to high-temperature oxidation tests will point out desirable oils. The obvious reason for this contradiction has been suggested above. The adherents of volatile naphthenic oils which show good burn-off characteristics seem to be concerned with engines which normally operate at oil consumptions low enough to take advantage of the clean-burning character of such oils. The adherents of the less volatile, generally oxidation-resistant paraffinic oils, by contrast, may be occupied with the lubrication of engines characterized by somewhat higher oil consumption and higher temperature, or by a more significant amount of crankcase oxidation.

In this discussion of ring-sticking phenomena only such data have been used in which it is believed that all variables were comparable except the one deliberately changed; those not familiar with such work might conclude that this condition is easy to attain. As a matter of fact, any one engaged in ring-sticking study should expect to spend a high proportion of his time in explaining to himself why his results do not check, and in locating unsuspected and uncontrolled variables. Ring-sticking is a very complex phenomenon, due in actual service to a variety of causes; it is doubtful whether any one laboratory test (engine or otherwise) can be devised to evaluate lubricating oils in a way which will correlate with all the variables in service.

## VARNISH.\*

The formation of varnish-like deposits, soluble in acetone and similar solvents, on engine parts, is not altogether a recent development. It has been known for years, and has usually been associated with the oxidation of oils of the sludge-forming type, and usually under conditions severe enough to cause accelerated deterioration. The fact that such deposits are being encountered in service is one indication that service conditions have become quite severe. There is not much doubt that oils differ in their tendency to form varnish. In our experimental work some years ago we encountered a striking comparison. Two oils of S.A.E. 40 viscosity were used in a prototype test engine under identical conditions and with the same amount of air fed into the crankcase. The figures for the two tests are as follows :—

	Oil A.	Oil B.
Time, hours . . . . .	50	50
Crankcase temp., ° F. . . . .	280	280
Neutralization number increase . . . . .	6.6	4.8
Saponification number increase . . . . .	25.1	18.3
Precipitation number increase . . . . .	0.02	1.6 †
Viscosity increase at 210° Saybolt sec. . . . .	686	2178
Carbon residue increase . . . . .	—	2.35
Condition of engine . . . . .	No crankcase, piston skirt, or ring deposits.	Crankcase sludged; all bearings and piston tightly cemented by varnish.

† This value was 3.6 at 40 hours; the decrease corresponds to rapid sludging.

An almost identical case was encountered in a comparison of two S.A.E. 20 oils of the same general type. A presumption of similarity, if not identity, for the sludge and the varnish from the unstable oil is afforded by the following data, obtained by micro-analysis :—

	Varnish.	Sludge.
Carbon, % . . . . .	74.6	73.1
Hydrogen . . . . .	6.9	6.7
Oxygen (diff.) . . . . .	17.8	16.2
Ash . . . . .	0.68	4.0

The higher ash content of the sludge might be due to the fact that the sample was obtained by scraping, whilst that of the varnish was recovered by solution in acetone.

\* The authors have not included, under the term "varnish" the orange-to-black, highly adherent and insoluble coatings associated with extremely high temperature operation. For these deposits, the authors have reserved the term "lacquer"; they suggest the distinction as a useful one.

In the spring of 1938 we had occasion to investigate a series of reclaimed motor oils. The occurrence of varnish with these materials was obviously related to their content of soluble oxidation products, and we were induced to continue the study with some new oils in order to connect the phenomena of our earlier observations. The work led us to conclude that the following are controlling factors in the early formation of acetone-soluble varnish in gasoline engines:—

(1) High crankcase oil temperature. The critical temperatures are in general about the same as those which will produce corrosive acids by oil oxidation.

(2) Oxidation of the oil to compounds which will ultimately drop out of solution as sludge. The amount of varnish deposited seems to be closely proportional to the amount of oxidation effected; interrupting the oxidation will stop the depositing of varnish after the supply of oxidized products has been exhausted.

(3) Adequate solvent power on the part of the lubricating oil for the oxidation products formed. The addition of 10 per cent. of preoxidized oil to a crankcase oil of low solvent power resulted, during the ensuing test run, in the formation of crankcase sludge, but no varnishing. The addition of 10 per cent. increments of preoxidized oil was repeated twice, with 10 hours of engine running between each addition. At the end of 35 hours the engine was badly sludged, but no varnish had been formed. The addition of 10 per cent. of the same preoxidized oil to a crankcase oil of high solvent power produced during the test run a copious varnish after 5 hours' operation, with no appreciable crankcase sludge. The high-solvency oil by itself had showed no varnishing until after 10 hours of running, which indicates that it took little, if any, part in the phenomenon.

As a further confirmation of this set of phenomena, the high-grade oil of low solvent power for sludge, mentioned above, was used in an experiment in which a completely filled filter cartridge of the cotton waste type was cut into the circuit. When this was done, the oil, which had produced no varnish by itself, yielded a slight but definite varnish deposit on the piston in 10 hours of operation. It thus appears that the presence of a contaminated filter cartridge in a lubricating system may serve as a source of varnish, even though the oil being used is of such a quality as not to cause trouble by itself.

(4) A high content of easily evaporated material in the oil medium. This may be the volatile neutral oil present in some S.A.E. 10 and 20 products, or may be heavy ends of gasoline coming in as fuel diluent. In the absence of any better explanation, it would seem that the light material evaporates off from the film of oil in contact with hot surfaces, concentrating the soluble oxidation products, which deposit as varnish; the process resembles the laying down of a shellac film when the alcohol solvent evaporates.

(5) Catalytic influences of materials in contact with the oil at high crankcase temperature. A comparison of several different bearing materials in the same engine, the oil and the test conditions being the same, gave the following:—

Bearing material.	Time, hrs.	Varnish.
Copper-lead . . . . .	10	Severe
Cadmium-silver . . . . .	10	Severe
Babbitt . . . . .	20	Slight

New bearing shells of identical size (to 0.0001 in.) were used for each test.

It is well known that oil deteriorates much faster in new engines than in those well conditioned by use; this is presumably due to the catalytic action of the fresh metal surfaces and particles. Similarly metallic soaps and other oil oxidation products will usually promote deterioration.\* These influences will accelerate lacquer deposition, and should be taken into account in both research and operating control.

All the above controlling factors have been closely related to the lubricating oil and its functioning; there are, however, several ways in which the gasoline fuel can share in the responsibility for engine varnish. These are all related to the fact that gasoline is not completely burned during starting and cold operation, particularly under light load. Under these conditions the unburned fuel consists of high-boiling fractions of the gasoline, somewhat oxidized by having been compressed with air in the compression stroke and then heated by direct contact with a flame. At these high temperatures the conventional gum inhibitors used in gasolines could not be expected to prevent oxidation. The heavy ends of cracked gasolines are themselves fair solvents for oil resins, and after oxidation of this sort are still better.† Furthermore, after oxidation of this sort it is evident that the unburned heavy fractions are potential sources of gum resins, since they contain aldehydes and probably peroxides.

These partly oxidized heavy fractions of gasoline may share in varnish formation in three ways:—

(a) They will pass down into the crankcase by migration past the piston rings, and accumulate in the crankcase. Each increment of diluent can be evaporated away from the oil by crankcase ventilating, and this may occur many times. But each time the diluent evaporates, its non-volatile gum content will be left behind, and in this way an appreciable concentration of soluble fuel gum can be built up in the crankcase oil. This functions in a manner analogous to that of the soluble resins and other products resulting from the oxidation of the oil itself, as discussed above; it deposits as varnish on metal surfaces when rendered insoluble by heating or by evaporation of the solvent.

(b) Once mixed with the oil, they will increase its solvent power for soluble oxidation products deposited (perhaps harmlessly) somewhere in the engine or in the oil filter. The influence of this sequence on varnishing has been discussed above.

\* The suspending action of some soaps may, of course, also be significant under certain conditions in hindering deposition.

† The back firing, through the carburettor of an engine running on gasoline with an extremely retarded spark, has been observed, in the authors' laboratory, to produce definite traces of phenol; phenol is a better solvent for resins than is gasoline, and this gives a picture of the improvement of solvent power by flame oxidation.

(c) Since these unburned materials are introduced above the piston, they have ample opportunity to come into contact with the piston crown and head carbon deposits formed in normal operation. When these deposits are laid down under conditions of low temperature operation, they contain a high proportion of partly burned oil, resins and asphaltenes, which serve as binders for the solids; as is well known, deposits of this type are characteristically soft and pasty. Diluent entering the crankcase under these conditions is likely to be saturated with unstable extracts from the carbon deposits, which can take part directly in the laying down of varnish.

#### OIL-RING CLOGGING AND STOKING.

Two very common types of lubrication trouble during the past few years have been winter sludging and the premature increase of oil consumption in engines apparently in otherwise good condition. This latter may occur at anywhere from 10,000 to 20,000 miles of use. Winter sludging is normally common only in operations where the ratio of idling time to miles travelled is very high, but the premature rise in oil consumption is very common for passenger automobiles generally. Strikingly enough, the difficulty does not seem to occur as soon in salesmen's cars, running 50,000 miles in a year, as it does in a carefully operated family car, used 6000 to 10,000 miles annually.

The two phenomena are perhaps more closely related than is apparent. The forming of winter sludge is correctly attributed to the emulsifying of oil and water by solid carbon-like materials (see photomicrograph, Fig. 2),\* and most writers on the subject, including the present authors, have assumed that the solid materials came down as fuel soot from partly burned gasoline.† A reanalysis of this condition, however, indicates that only very small amounts of fuel soot are likely to be available in equipment which produces large amounts of winter sludge; for instance, rubbish-collecting trucks which idle steadily during the greater part of an eight-hour trip covering 14-18 miles. Under these conditions the engine will be warm, even though the crankcase may be cool, and not much soot can be expected to form by chilled combustion. In a fleet operated under the authors' observation the collecting of water in the crankcases has been avoided by suitable control of temperature. However, the accumulating of carbonaceous material has continued, but only in proportion to the oil consumption of the individual engines. Units showing large amounts of solids in the crankcases and valve compartments invariably showed high oil consumption also. From this it seems more probable that the solid materials (which would serve as emulsifiers for winter sludge if water were present) came from the wash-down of partly coked oil and "carbon" deposits formed above the piston; the carrying medium is the oil returning to the crankcases under conditions of high oil consumption. This is according to the discussion of low-temperature ring-fouling given by the authors in the 1937 A.S.T.M. paper mentioned above.‡

\* By courtesy of L. W. Vollmer, Gulf Research and Development Company.

† Gruse and Livingstone, A.S.T.M. Symposium on Lubrication, 1937, p. 1.

‡ *Loc. cit.*, p. 10.

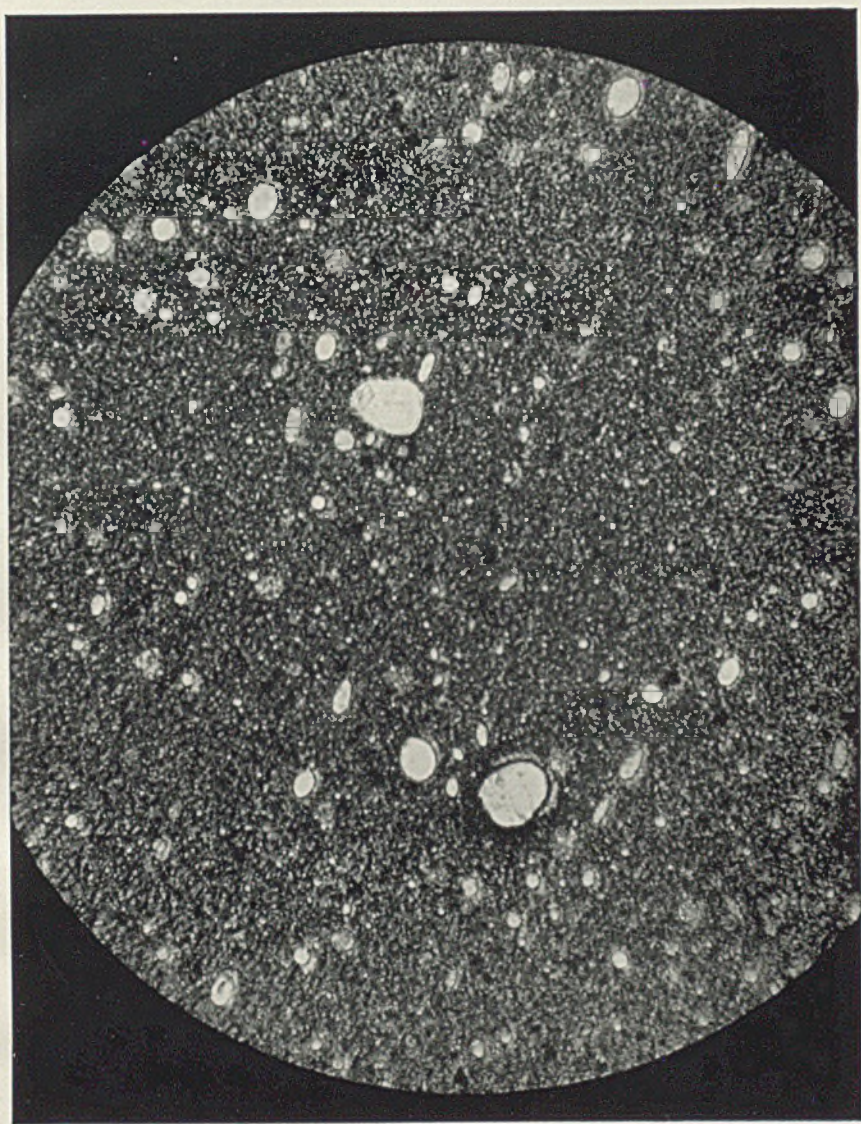


FIG. 2.  
PHOTOMICROGRAPH (400 X) OF WINTER SLUDGE.

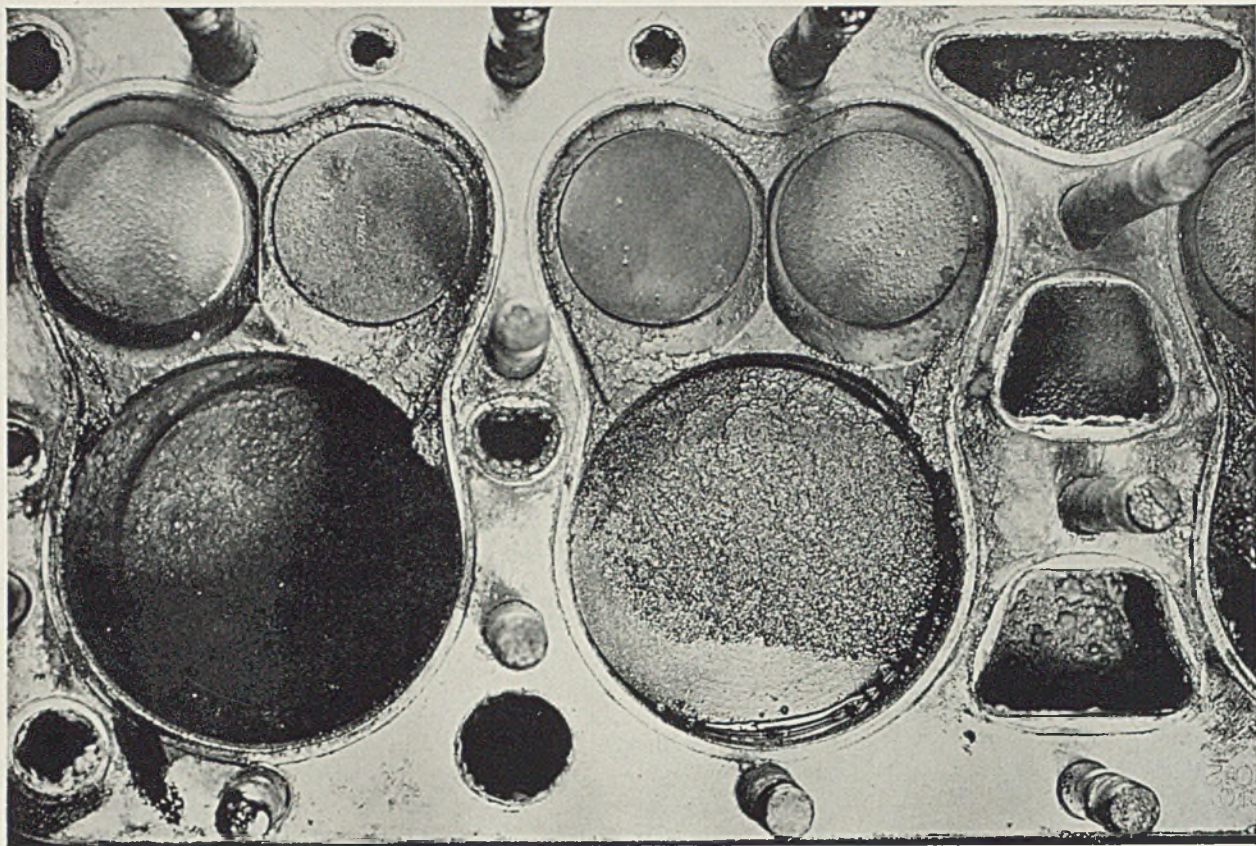


FIG. 3.

PHOTOGRAPH OF PISTON IN "V" TYPE ENGINE SHOWING OIL WASHING OF PISTON WITH HIGH OIL CONSUMPTION. A SMALL POOL OF OIL HAS FORMED AT THE LOWER EDGE OF THE PISTON.



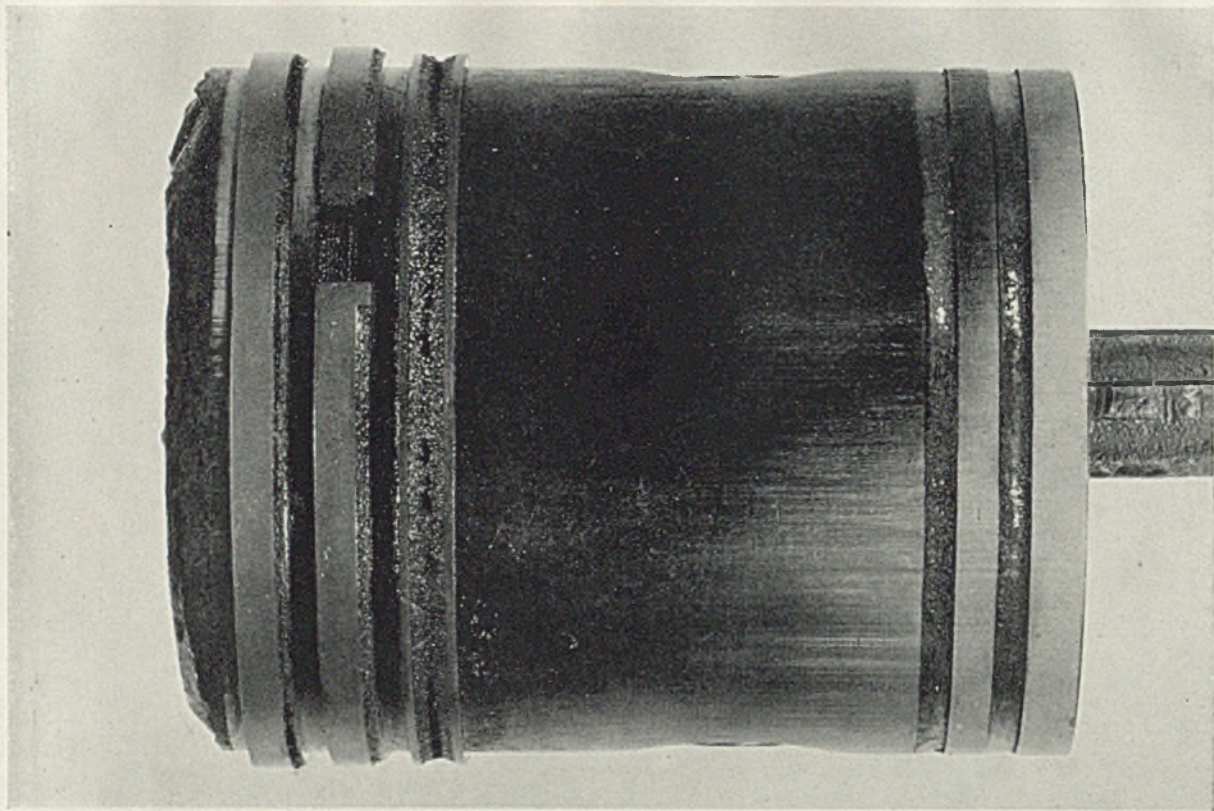


FIG. 5.

PHOTOGRAPH OF PISTON FROM EXPERIMENTAL ENGINE AFTER 40 HOURS OF OPERATION ON OIL B (SEE TEXT).

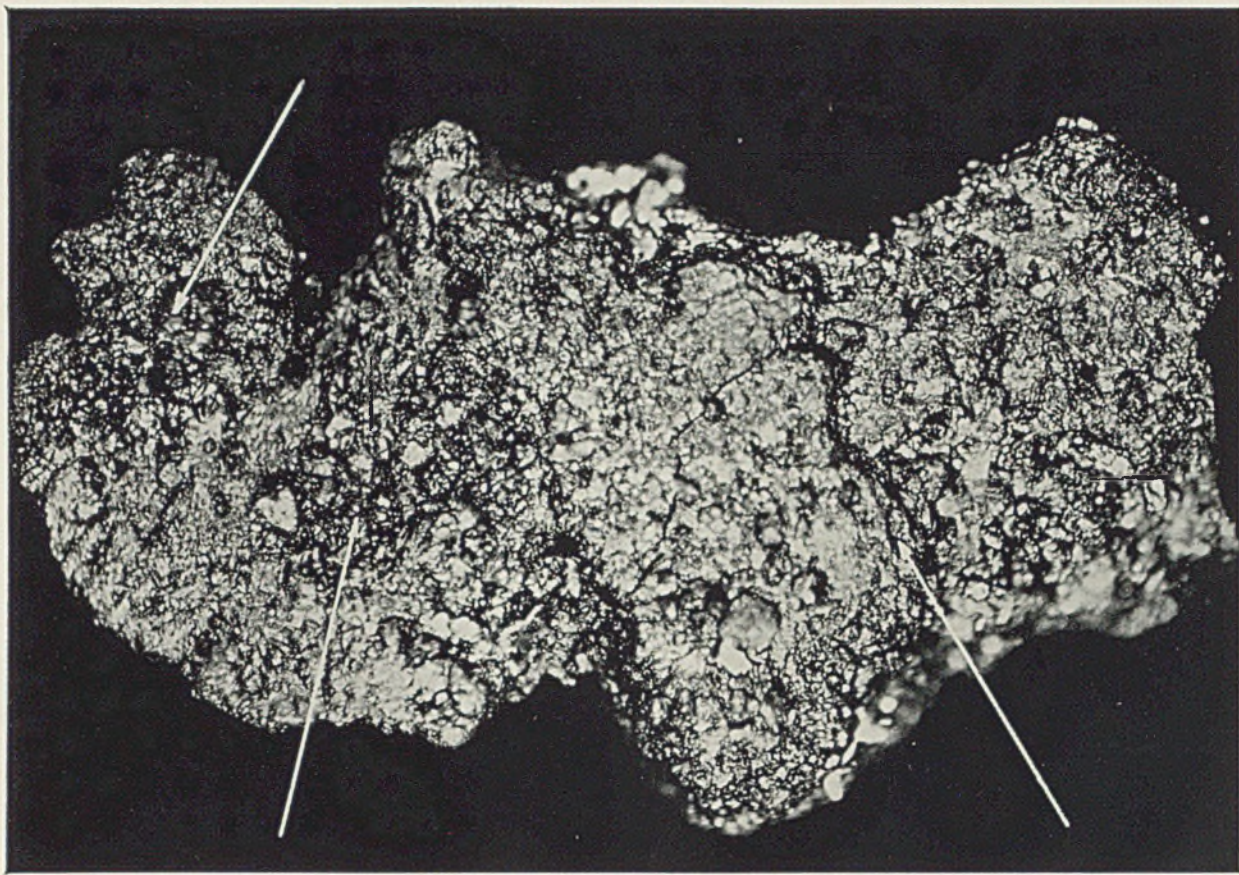


FIG. 6.

25  $\times$  ENLARGEMENT OF A SMALL CHIP TAKEN FROM A FEATHER EDGE AT THE TOP OF THE PISTON USED IN THE TEST WITH OIL C (SEE TEXT). ARROWS POINT TO AREAS SHOWING GLOBULAR FORMATION WHICH INDICATE THE DEPOSIT WAS MOLTEN WHEN HOT.

The operation of such a washing action is indicated in the accompanying photograph (Fig. 3). The normal deposit, which might be expected to form over the entire piston surface, has been washed away on the low side of the piston of a "V" type engine, leaving clean metal. A small pool of the washing oil can be seen at the edge of this piston. The combustion chamber deposits formed under conditions of low temperature and part load are well known to be of the soft and pasty variety. They are made up of 20-45 per cent. liquid oil, about 10 per cent. asphaltenes and resins, and the rest coke, lead and ash.\* Such wet mixtures are easily extracted and disintegrated by hot oil. Hot unburned gasoline residues from starting, choked operation and running under very light load, will begin the process of washing this down off the piston crown into the ring grooves. Only very small particles can pass the rings, because of a combination of grinding and edge filtering. When the wash-down material reaches the oil ring-slots and piston drain-holes it has cooled somewhat, and apparently some of the resins come out of solution on the walls of the slots; this is indicated by inspection of oil rings which have been clogged. This resin layer then acts as an adhesive to bind solid particles from the disintegrated piston crown material. As pointed out in our 1937 paper, the build-up proceeds from the outside towards the inside of the slots. Experiments in our laboratory have led us to believe that the binder in the low-temperature carbon deposits resembles closely conventional oil varnish, and the ring clogging under discussion depends on a transfer of this binder from piston-crown to ring-groove slots. Since the slots and drain holes were originally provided to permit return of oil to the crankcase, the clogging of these passages interferes with the normal action of the oil control rings, and oil consumption increases. Once complete clogging has occurred it is practically impossible to clean the oil-control system in any way except by mechanical cleaning. If this explanation is correct, there is considerable danger that certain types of solvent "carbon removers" might be responsible for a good deal of ring-clogging trouble, since they may dissolve the carbon binder and wash it down the sides of the piston.

Once rings are clogged, oil consumption increases and the condition goes from bad to worse. The ring-clogging discussed above can be largely attributed to solvent and mechanical action exerted on deposits formed above the rings. There is, however, another set of causes and events which leads to the same result and which occurs under conditions of efficient high-temperature operation when the piston crown remains more or less clean. The starting-point for this sequence of engine trouble is the varnishing of the surfaces in the vicinity of the oil ring groove. In the course of our study of engine varnishes we encountered a series of results in which varnish deposit was not severe enough to cause piston-sticking, but did bring about a very marked increase of oil consumption. Two oils were compared: one was an S.A.E. 20 paraffinic oil with low resistance to sludging, and the other was an S.A.E. 30 naphthenic oil containing a

\* These figures are from deposits in experimental engines. Even short operation at higher temperature will dry the deposits, bringing them nearer to—

Liquid oil . . . . .	10-20%
Asphaltenes and resins . . . . .	2-5
Coke, lead and ash . . . . .	80-85

viscosity index improver. The inspection data on the two are given as follows :—

	Naphthenic blend.	Paraffinic oil.
Specific gravity . . . . .	0.8827	0.869
Viscosity at 100° F. . . . .	490	354
Viscosity at 210° F. . . . .	64.1	57.4
V.I. . . . .	102	110

When operated under identical test conditions of accelerated oxidation, the two oils gave results indicated in the accompanying Fig. 4. It will

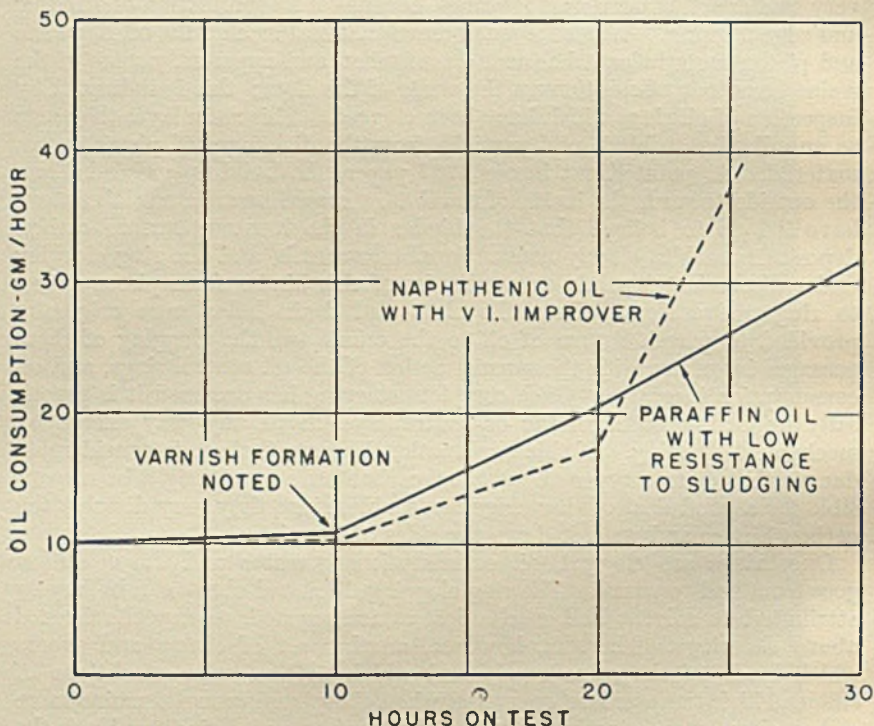


FIG. 4.

be observed that oil consumption stayed low to the point at which varnish deposition around the oil ring grooves was noted. Oil consumption then increased rapidly to the end of the test without any further marked indication of additional varnishing. Under comparable conditions, other oils showing high resistance to varnishing went through the entire test period without any increase of oil consumed per hour. No ring clogging was encountered in any of these latter cases because the engine was being operated with extremely high output; all oil passing the rings was burned cleanly in the combustion chamber. If a cycle of low load operations had been introduced at this point, oil-ring clogging would be expected to occur.

In order to study the sequence further, the work was transferred to another engine characterized by low crankcase temperature and absence of crankcase oxidation; the device was adopted of supplying oils pre-oxidized to different extents. An S.A.E. 40 solvent-refined naphthenic oil, preoxidized in an iron apparatus at 280° F. to the following test values, was employed :—

Neut. number	. . . . . 0.54	Naph. insol.	. . . . . 0.081%
Sapn. number	. . . . . 5.7	Chloroform sol. from naph.	
		insol.	. . . . . 0.027%

The results may be tabulated as follows :—

Hours on test.	Oil consumption, gm./hour.	Varnish around oil-ring groove.
20	2	Slight
40	3	No change
60	3.5	No change
80	3.5	No change

It is evident that no further varnishing and no increase in oil consumption occurred with long-extended running. The explanation apparently was that the supply of oxidation products contributing to varnish deposition had been exhausted during the first 20 hours of running. The test was repeated, but at the 40-hour period the crankcase was drained and a second filling of the same preoxidized oil was supplied. The results are as follows :—

Hours on test.	Oil consumption, gm./hour.	Varnish around oil-ring groove.
20	4.7	Slight.
40	4.8	No change.
Oil changed; preoxidised oil again supplied.		
60	3.2	Heavy.
80	10.3	Ring slots partly clogged.
90	6.5 *	Ring clogged and stuck; cylinder scored.

\* The decrease of oil consumption after 80 hours is striking and seems contradictory; however, it is believed to be due to the sharp increase of blow-by at this stage.

The inspection of the remaining crankcase oil showed no marked change from the values given above, except a 35 per cent. decrease of saponification number. Evidently in this case the saponifiable constituents served as a source for the varnish deposits.

This sequence was then repeated three times in a somewhat different way. A new base oil was used in each case, and 10 per cent. increments of a preoxidized oil were added to it at 20-hour intervals with inspections at each 10-hour point. The base oils were :—

- (a) A highly refined paraffinic, S.A.E. 30,
- (b) A solvent-extracted Mid-Continent, S.A.E. 30,
- (c) A solvent-extracted naphthenic, S.A.E. 30,

respectively. The preoxidized material added was a solvent-refined Mid-Continent S.A.E. 10 oil, run in a test engine under high output and with crankcase oxidation at 280° F.; the oxidation run was carried to the point of varnish formation. The inspection data for this addition oil are as follows:—

Neut. number . . . . .	4.4	Naph. insol. . . . .	0.902%
Sapn. number . . . . .	23.1	Chloroform sol. from naph. insol. . . . .	0.808%

In all three cases the set of phenomena repeated itself, varnishing and oil-ring clogging occurring in turns, but in 40–50 hours instead of 80, presumably because the addition material had been more drastically oxidized. The accompanying Fig. 5 shows the piston from the B test (solvent-extracted Mid-Continent base oil) after 40 hours of running; the other pistons were almost exact duplicates. The heavy varnishing, the clogging of oil-ring slots, and the build-up of decomposed varnish around the compression ring grooves and the top edge of the piston are easily observed. The fact that the varnish material may be molten when deposited is indicated by the photomicrograph given in Fig. 6.\* This is a 25× enlargement of a chip taken from a feather edge at the top of the piston used in the C run above. Typical indications of a molten condition are indicated by the arrows; the whole resembles to some extent a chilled lava or clinker of fusible material.

The inspection data on the used oils drained from the engine at the end of each test are as follows:—

	Oil A.	Oil B.	Oil C.
Viscosity at 100° F. . . . .	512	548	488
Neutralization number . . . . .	0.57	0.58	0.66
Saponification number . . . . .	4.5	5.3	4.8
Naphtha-insoluble, % . . . . .	0.196	0.156	0.149
CHCl <sub>3</sub> -soluble . . . . .	0.139	0.121	0.092

These results are all of the same order of magnitude because the preoxidized oil added to each was in all three cases identical.

The entire set of data indicates that the phenomena are due to the decomposing of soluble oxidation products on hot surfaces. The various sources for varnish deposited on pistons, listed earlier in this paper, can presumably contribute equally to this form of varnishing, and thus cause serious interference with the functioning of the devices set up for control of oil consumption.

#### CONCLUSION.

The general effect of the work presented here is to indicate that engine-varnishing, ring-sticking, and oil-ring clogging are more or less closely related. Oxidation of the oil, chiefly in the crankcase, to unstable products, followed by the decomposing of these products at hot points in the engine, follow an important part in all three.

\* By courtesy of L. W. Vollmer, Gulf Research and Development Company.

It is recognized that increased outputs necessarily involve higher piston and cylinder-wall temperatures. However, it does not seem necessary that crankcase temperatures must also be higher. Since the effect of increased temperature on rate of oxidation is enormous—a 20° F. rise means approximately a doubling of the oxidation rate—every decrease in crankcase temperature means a real improvement. While it is true that the oil is exposed to more severe conditions for short time periods, it must be remembered that the bulk of the oil spends most of its time at the crankcase temperature. It seems reasonable, therefore, to hope that engine designers can arrange to keep crankcase oil temperatures low. They will thus take an unnecessary load off the oil, leaving it in better condition to carry the necessary load it encounters on the piston, cylinder walls, and bearing surfaces.\*

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\* It is believed that these remarks apply to all oils, whether or not compounded, inhibited or otherwise altered by additive agents.

## STUDIES ON THE SEPARATION OF PARAFFIN WAXES.\* PART II—PHASE RELATIONSHIPS.

By M. F. SAWYER, Ph.D., A.M.Inst.Pet., T. G. HUNTER, D.Sc., Ph.D.,  
M.Inst.Pet., and A. W. NASH, M.Sc., F.Inst.Pet.

It has been mentioned in Part I that the only available method for the elucidation of the wax equilibrium diagram involves the separation and analysis of the solid and liquid equilibrium phases formed at temperatures within the melting range of the wax stock.

### APPARATUS FOR EQUILIBRIUM EXPERIMENTS.

The apparatus used throughout these equilibrium experiments is illustrated in Fig. 1.

Constructed in brass, it consists essentially of three sections :—

- (1) the cylinder *AB* of diameter 5 cm. and length 14 cm., which is screwed into
- (2) the cylinder head *CD*, through which passes the screw *E* carrying the piston head *F*, and
- (3) the conical cylinder head *G*.

The piston *F* consists of a brass plate with a rubber washer, the purpose of the latter being to prevent seepage of the liquid phase between the piston and the cylinder wall. The conical cylinder head *G* contains a perforated brass filter plate *HI* of diameter 4.7 cm. and thickness 4 mm., on which is placed a layer of thin canvas *L*, which, in turn, is covered with a layer of filter-paper. The liquid phase passing through the filter-plate was collected in a Buchner flask attached to the conical cylinder head by means of a rubber bung at *K*. All screw connections were made water-tight by the use of Mobilgrease Water-pump Grease No. 6.

### EXPERIMENTAL PROCEDURE.

The portion of the apparatus described under (1) and (2) above was assembled in an inverted position with the wheel handle pointing downwards, and placed in a thermostat of 10 gallons capacity. The thermostat was of the normal electrically controlled type, and the bath temperature was easily maintained to within  $\pm 0.05^\circ$  C., an accuracy that was considered adequate for the purpose. The apparatus, which was maintained in the inverted vertical position by means of a cradle support attached to the inside of the bath, was allowed to attain the thermostat temperature, and the molten wax sample, normally of 70–80 grams, was then poured from a glass beaker into the cylindrical section of the apparatus. The liquid was stirred occasionally during the initial stages of cooling, but stirring was

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\* Paper received April 1940.



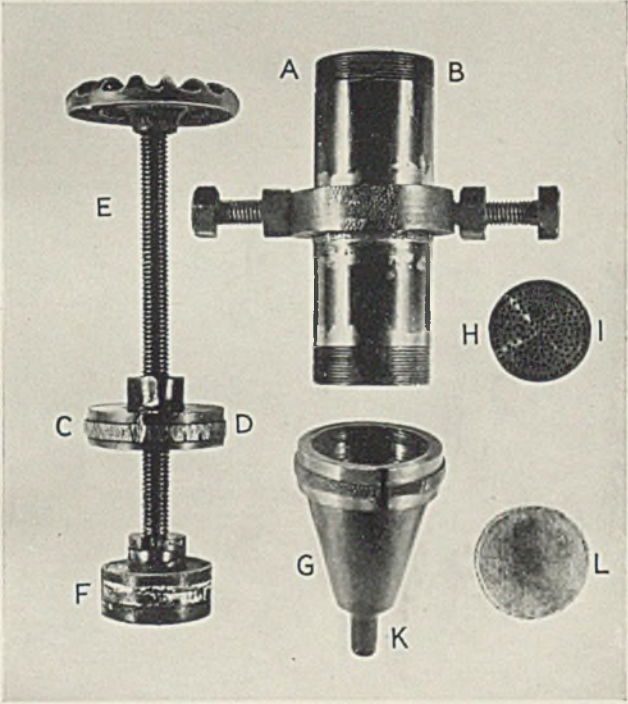


FIG. 1.

almost continuous from the time solid wax first appeared until the liquid/solid wax mixture had cooled to the equilibrium or thermostat temperature. After reaching this temperature the mixture was allowed to stand for a further 6 hours, during which time stirring was intermittent. At the end of this period the conical cylinder head with Buchner flask attached was screwed into position at *AB*. The apparatus was then completely immersed in the thermostat and allowed to remain in this position for 1 hour, so that the whole apparatus attained the bath temperature. The apparatus was then momentarily taken from the thermostat, *inverted*, and immediately replaced in the cradle support which had been so designed that the whole

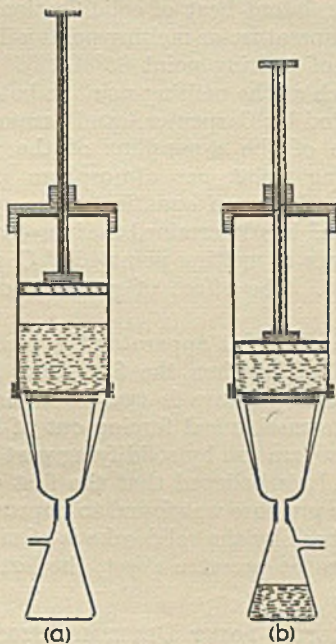


FIG. 2.

apparatus (except for a portion of the screw *E*) was immersed whilst being supported in the position shown in Fig. 2.

Pressure was then applied to the solid/liquid equilibrium mixture by slowly turning the screw *E*. This procedure was continued until it was found impossible to turn the screw further. This operation was carried out over a period of 30–45 minutes, following which the apparatus was allowed to remain in the thermostat for a further period of 2 hours, the screw *E* being maintained in the position of maximum pressure. The apparatus was then taken from the thermostat, the Buchner flask containing the liquid phase removed from the conical cylinder head *G*, and the conical head separated from the cylinder by disconnecting at *AB*. The solid phase was removed from the cylinder as a solid block by turning the screw *E*. The amount of liquid phase was determined by weighing the Buchner

flask before and after the experiment. The melting point of each phase was found in the manner described later.

Fig. 2 illustrates respectively the set-up of the apparatus (*a*) immediately preceding the separation of the two phases, and (*b*) on completion of the separation.

Since pressure was employed to assist phase separation, the effect of such pressure on the solid-liquid equilibrium must be considered. This may be predicted by Le Chatelier's principle. When the pressure on a solid and liquid in equilibrium at the melting point is increased, the phase with the larger specific volume tends to disappear. In this case liquid paraffin wax has the greater specific volume, and pressure will cause some of the liquid to solidify, latent heat of solidification will be evolved, and the new equilibrium temperature or melting point will be higher.

Taking three waxes of melting point  $65^{\circ}$  C.,  $56^{\circ}$  C., and  $44.5^{\circ}$  C. the specific volumes of which at the melting point in both the liquid and solid states have been reported by Carpenter,<sup>1</sup> and assuming their latent heats of fusion to be those of the *n*-paraffins of the same melting point,<sup>2</sup> the increase in melting point per atmosphere pressure increase has been calculated by the Clapeyron equation to be approximately  $+0.01^{\circ}$  C./atmosphere. Bunsen<sup>3</sup> has determined the increase in melting point with pressure of a paraffin wax of melting point  $46.3^{\circ}$  C. and reports a value of  $+0.036^{\circ}$  C./atmosphere. The effect of pressure on the equilibrium is obviously small.

During actual filtrations in this apparatus the pressure applied is small, but is increased considerably when the filter-cake is pressed to remove liquid. The effect of this pressure is two-fold: first to improve solid-liquid separation by the mechanical forcing out of liquid from the cake, and secondly to retard separation by solidifying part of the liquid wax still retained by the cake. It is believed that the first effect more than outweighs the second, since pressure was found to improve the separation, and as retention of liquid phase by the solid cake is of more importance in the equilibrium results than the pressure effect, the latter may be ignored in comparison.

#### MELTING-POINT DETERMINATION.

The melting points were determined by the following method, for which only 5 grams of the sample were required. A  $\frac{3}{4} \times 8$  inch glass test-tube was filled to a mark ( $1\frac{1}{2}$  inches from bottom) with the wax sample and placed in an air-jacket consisting of a larger glass boiling tube ( $1\frac{1}{2} \times 6$  inches), which, in turn, was placed in a 3-litre beaker containing water at a temperature  $10$ – $15^{\circ}$  F. lower than the expected melting point of the sample. An N.P.L. Standardized I.P.T. Wax Setting-point Thermometer was placed in the molten sample so that the thermometer bulb reached to within  $\frac{1}{4}$  inch of the bottom of the test-tube. A cooling curve was then plotted, the temperature being taken at half-minute intervals, starting at a temperature  $5^{\circ}$  F. above the melting point of the wax, and continuing until the first minimum cooling rate had been passed. The melting point was taken as that temperature at which five or more identical consecutive readings were observed. Taking all precautions mentioned in the I.P.T. method, Serial Designation-PS 11a, regarding the heating

of the sample, duplicate results are obtained differing by not more than  $\pm 0.05^\circ \text{F}$ .

For the purposes of this research the melting point of paraffin wax is therefore defined as the temperature at which molten paraffin wax, when allowed to cool under the conditions specified above, first shows the minimum rate of temperature change. The values determined in this way will be referred to hereafter as I.P.T. melting points.

#### EXPERIMENTS WITH DE-OILED SLACK WAX.

The first series of experiments designed to give some indication of the form or nature of the equilibrium diagram were made with a wax stock consisting of de-oiled slack wax of I.P.T. melting point  $114.0^\circ \text{F}$ . Equilibrium experiments were conducted over the temperature range  $91.3^\circ$ – $108.7^\circ \text{F}$ . in the manner described above. In each case the yields and I.P.T. melting points of the solid and liquid phases were determined, with the results shown in Table I below :—

TABLE I.

Experiment.	Equilibrium temperature, $^\circ \text{F}$ .	% by Weight.		I.P.T. melting point.	
		Solid phase.	Liquid phase.	Solid phase, $^\circ \text{F}$ .	Liquid phase, $^\circ \text{F}$ .
1	91.3	89.1	10.9	117.2	91.0
2	96.1	78.2	21.8	119.3	96.0
3	97.9	75.6	24.4	119.8	97.7
4	99.6	72.1	27.9	120.0	99.3
5	103.4	58.1	41.9	122.5	103.2
6	104.5	54.5	45.5	123.0	104.3
7	108.7	33.2	66.8	125.7	108.6

These results are shown graphically in Fig. 3, which can be provisionally considered to represent equilibrium between the two phases formed by the wax stock at temperatures within its melting range.

In this figure the ordinate and abscissa represent equilibrium temperature and I.P.T. melting point respectively. The "liquidus curve" on the left was obtained by plotting the I.P.T. melting point of the separated liquid phase against the equilibrium temperature, whilst the "solidus curve" on the right was obtained by plotting the I.P.T. melting point of the separated solid phase against equilibrium temperature. This diagram represents graphically the experimentally determined phase relationships. In experiment 4, for example, the stock wax was maintained at a temperature of  $99.6^\circ \text{F}$ ., indicated on the figure by point  $M^1$ .

The stock wax under these conditions  $M$  was separated into a liquid phase  $L$  of I.P.T. melting point  $L^1$  equal to  $99.3^\circ \text{F}$ ., and a solid phase  $S$  of I.P.T. melting point  $S^1$  equal to  $120^\circ \text{F}$ . It is believed, however, that the experimentally prepared solid phases were not entirely free from liquid phase retained mechanically in the solid.

The complete removal of such entrained liquid phase is exceedingly difficult, and the actual phase separation obtained was the best possible

with the facilities available, and hence the diagram, while not representing true equilibrium, is the nearest possible approach to it. In true equilibrium the solidus curve would undoubtedly be displaced somewhat to the right of that in the figure.

If the equilibrium curve is analogous to that for a continuous series of solid solutions formed by two pure components as described in Part I, then the diagram should be applicable to a multi-stage removal of liquid at different temperatures. Thus, the solid phase of I.P.T. melting point  $119.3^{\circ}\text{F}$ . from experiment 2 (Table I), if allowed to attain equilibrium at a temperature of  $104.5^{\circ}\text{F}$ ., should produce a solid phase of I.P.T. melting point  $123.0^{\circ}\text{F}$ ., for in experiment 6 the equilibrium temperature of  $104.5^{\circ}\text{F}$ . produced a solid phase of this I.P.T. melting point. Accordingly, the solid phases resulting from experiments 1, 2, and 3 were in each case

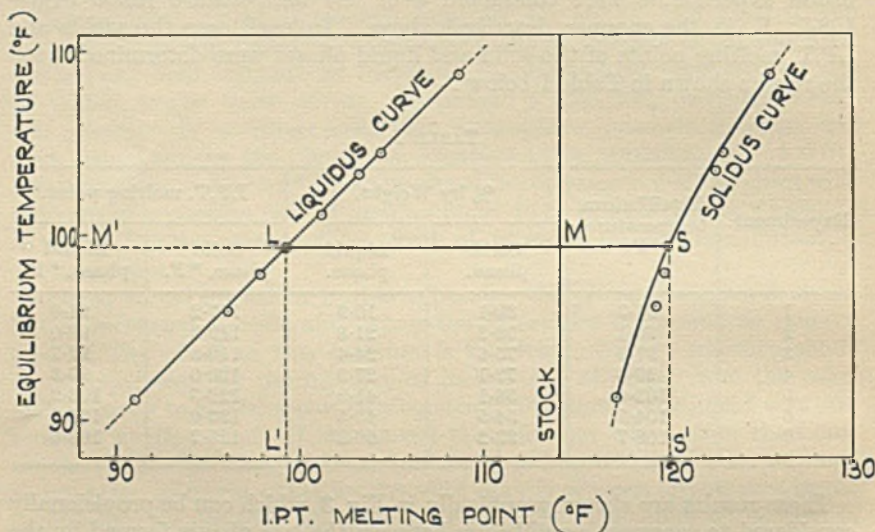


FIG. 3.

allowed to reach equilibrium at a higher temperature, after which the liquid phase was removed in the usual manner. The results of these three two-stage experiments are given in Table II (p. 435), under experiments 1(a), 2(a), and 3(a) respectively.

The results from each of these two-stage processes are summarized in Table III (p. 435), and also compared with the appropriate one-stage experiment.

It will be noted from Table III that a one-stage removal of liquid phase from the original stock at an equilibrium temperature of  $103.4^{\circ}\text{F}$ . resulted in a solid phase of I.P.T. melting point  $122.5^{\circ}\text{F}$ ., whereas for a final equilibrium temperature of  $103.5^{\circ}\text{F}$ . in the two-stage process a solid of I.P.T. melting point  $120.6^{\circ}\text{F}$ . was obtained. Similar results are observed when the solid phases obtained in experiments 2(a) and 3(a) are compared with that obtained in a one-stage removal of liquid at the equilibrium temperature of  $104.5^{\circ}\text{F}$ .

TABLE II.

Experiment.	Expt. No.	Equilm. temp., ° F.	% by wt. Solid.	% by wt. Liquid.	I.P.T. M.Pt. Solid, ° F.	I.P.T. M.Pt. Liquid, ° F.
First Stage. Expt. 1. Table I . . . . .	1	91.3	89.1	10.9	117.2	91.0
Second Stage . . . . .	1(a)	103.5	77.6	22.4	120.6	103.4
First Stage. Expt. 2. Table I . . . . .	2	96.1	78.2	21.8	119.3	96.0
Second Stage . . . . .	2(a)	104.9	85.4	14.6	121.6	104.6
First Stage. Expt. 3. Table I . . . . .	3	97.9	75.6	24.4	119.8	97.7
Second Stage . . . . .	3(a)	104.5	88.7	11.3	121.4	104.2

TABLE III.

Expt.	Equilibrium temp. ° F.	Solid Phase.	
		% by Weight.	I.P.T. Melting point, ° F.
1 and 1(a) 5	103.5*	69.0	120.6
	103.4	58.1	122.5
2 and 2(a) 6	104.9*	66.8	121.6
	104.5	54.5	123.0
3 and 3(a) 6	104.5*	67.0	121.4
	104.5	54.5	123.0

\* Equilibrium temperature of second stage.

It is apparent from these experiments that a two-stage process results in a solid phase of lower I.P.T. melting point than that obtained in a one-stage experiment on the original stock at the higher of the two equilibrium temperatures. The results of the three two-stage experiments are illustrated in Fig. 4, in which *AB* is the solidus curve of Fig. 3. It would appear that an equilibrium diagram similar to that shown in Fig. 3 applies only to a one-stage fractional melting process, and that it is not applicable to a multi-stage fractional melting process for the separation of paraffin waxes.

The fact that the solid phase obtained in the second stage of a two-stage process does not fall on the "solidus curve" of the equilibrium diagram could be explained by the incomplete separation of the liquid and solid phases, some liquid phase being retained by the solid phase, and hence lowering its I.P.T. melting point. Assuming that I.P.T. melting point follows the mixture rule, the amount of liquid phase retained in this way by each two-stage solid may be estimated. Thus, it has been calculated

that a 10 per cent. retention of liquid (expressed as a percentage of the solid phase) would account for the difference in I.P.T. melting point between the one-stage and two-stage solid phases obtained at the same equilibrium temperature in experiments 1(a), 2(a), and 3(a). In these three experiments the phase separations were all carried out in a similar manner at nearly constant temperature ( $103.5\text{--}104.5^\circ\text{F}$ ). Equilibrium experiments conducted in the same equipment at a constant temperature of  $81^\circ\text{F}$ . in which the solid and liquid phases were wax and a solution of wax in toluene respectively indicated that the percentage retention of liquid by solid phase

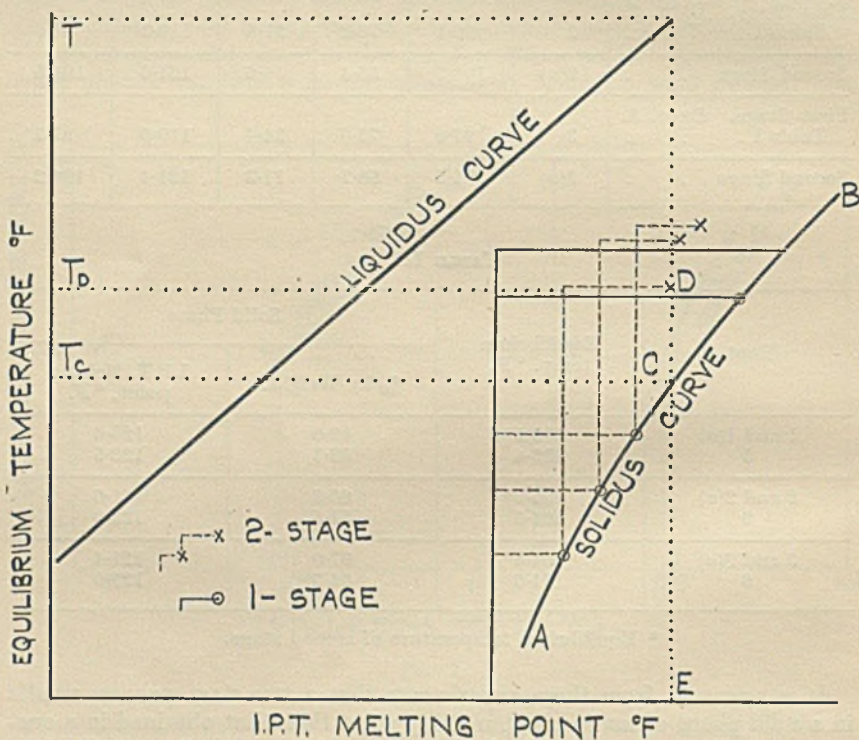


FIG. 4.

was, as shown in Fig. 5, a function of the ratio solid phase/liquid phase. It will be seen from this figure that for the same solid/liquid ratios as those prevailing in experiments 1(a) to 3(a), viz. 3.5, 5.9 and 7.9 respectively, the percentage retention is nearly constant, as was the case with the calculated values for these experiments. The actual percentage retentions are not, of course, comparable, owing to the differences in the liquid phases. This would suggest that retention of liquid phase by solid phase could account for the difference between the one-stage and multi-stage "solidus curves."

Another explanation of the observed phenomenon is possible. In Fig. 4 the two waxes C and D have the same I.P.T. melting point—namely, E. On heating, wax C begins to melt at temperature  $T_c$ , whilst wax D

commences melting at the higher temperature  $T_D$ . Both waxes are completely molten at temperature  $T$ . Although both waxes have the same I.P.T. melting point, they have different melting ranges, wax  $C$  melting over the range  $(T_C - T)$  and wax  $D$  over the range  $(T_D - T)$ , and hence different compositions. Even if the stock wax consisted simply of some half dozen  $n$ -paraffins, it is obvious that, completely independent of liquid phase retention, two solids could be obtained from it having the same I.P.T. melting point, but of different composition, and of course different

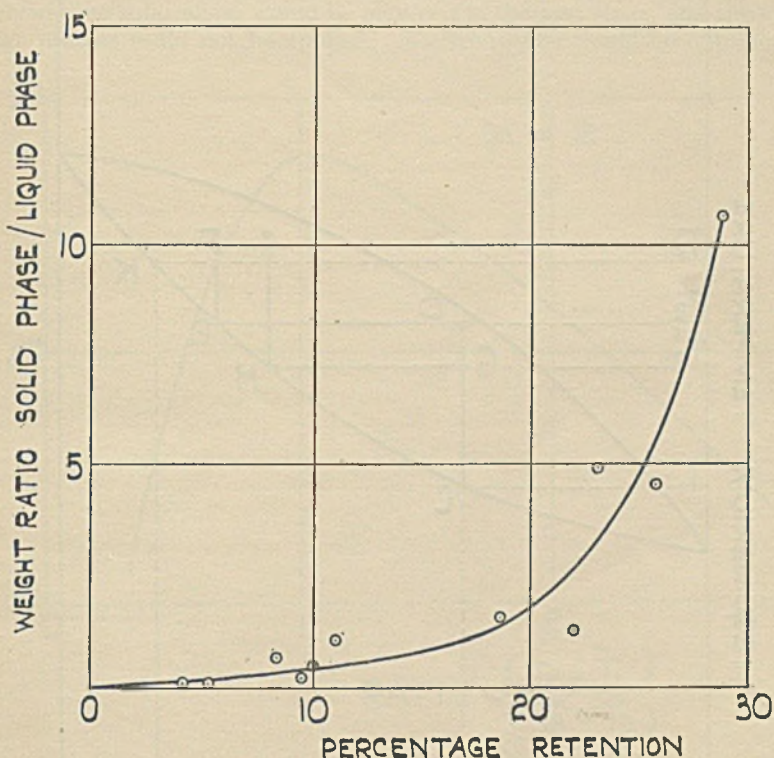


FIG. 5.

melting ranges. It is conceivable that a very large number of solid phases having identical I.P.T. melting points but different compositions could be obtained from even such a simple stock. Indeed, it is obviously possible, as was explained in Part I, to obtain a very large number of solid phases of identical molecular weight, or of identical melting point, density or other physical property, but differing compositions. In fact, the only satisfactory diagram for representing equilibrium in a system of  $n$  components is one showing  $n-1$  composition variables or  $n-1$  physical property variables. The major reason for the lack of coincidence of the one- and two-stage solidus curves is probably to be found in the method of representation, where the phases of a multi-component system are inadequately characterized in



terms of a single physical property variable, with retention of liquid phase by solid phase as an additional complication.

### THE "SWEATING" PROCESS OF FRACTIONAL MELTING.

An equilibrium diagram of the continuous solid solution type applying to the pure substances *A* and *B* is illustrated in Fig. 6. Consider a mixture

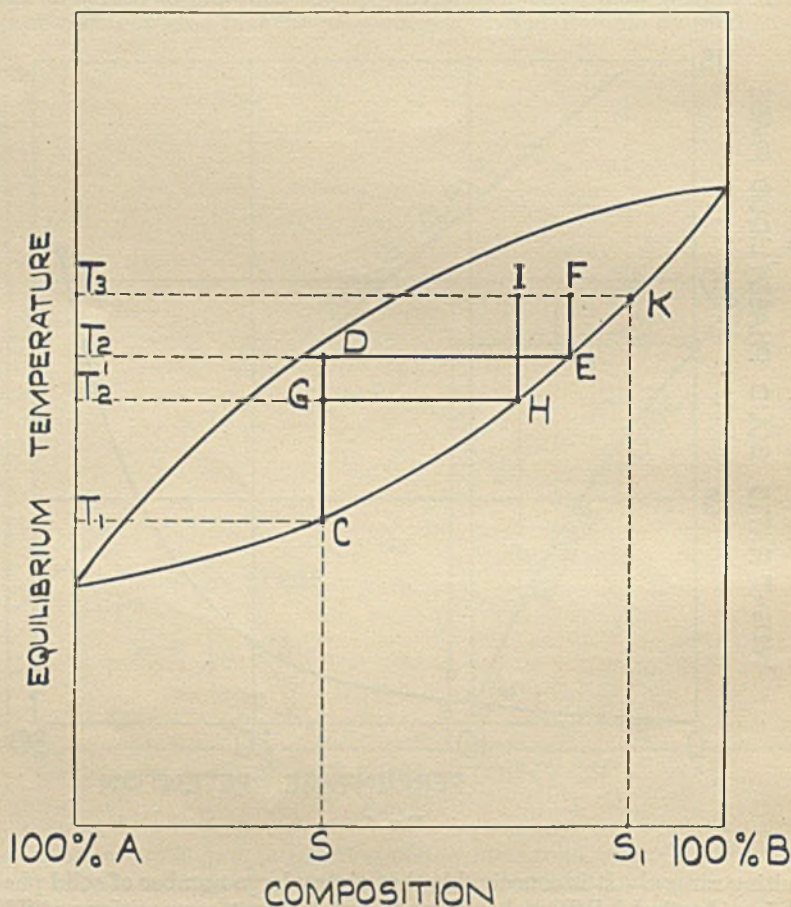


FIG. 6.

of *A* and *B* of composition *S* from which a solid of composition *S*<sub>1</sub> is to be prepared, by two-stage fractional melting over the temperature range *T*<sub>1</sub> to *T*<sub>3</sub>.

The two-stage process may be carried out in two ways. First the temperature of the stock may be raised from *T*<sub>1</sub> to *T*<sub>2</sub>, and after attaining equilibrium, the liquid phase is separated, then the temperature of the solid phase *E* may be raised to *T*<sub>3</sub> and the equilibrium liquid phase separated,

as illustrated by the steps  $C D E F K$ , where the temperature rise  $T_1$  to  $T_2$  is not equal to the temperature rise  $T_2$  to  $T_3$ —that is, two stages of unequal temperature increments have been employed. In the second method, illustrated by the steps  $C G H I K$ , the two temperature rises  $T_1$  to  $T_2'$  and  $T_2'$  to  $T_3$  are equal. That is, two stages of equal temperature increments have been employed. It is obvious, of course, that the two stages of unequal temperature increments can be carried out in a very large number of different ways. The first-stage temperature increment must, of course, be smaller than the melting range of the original stock, otherwise no solid phase would be obtained in the first stage, and the two-stage process could not be applied. Similar results would be obtained if

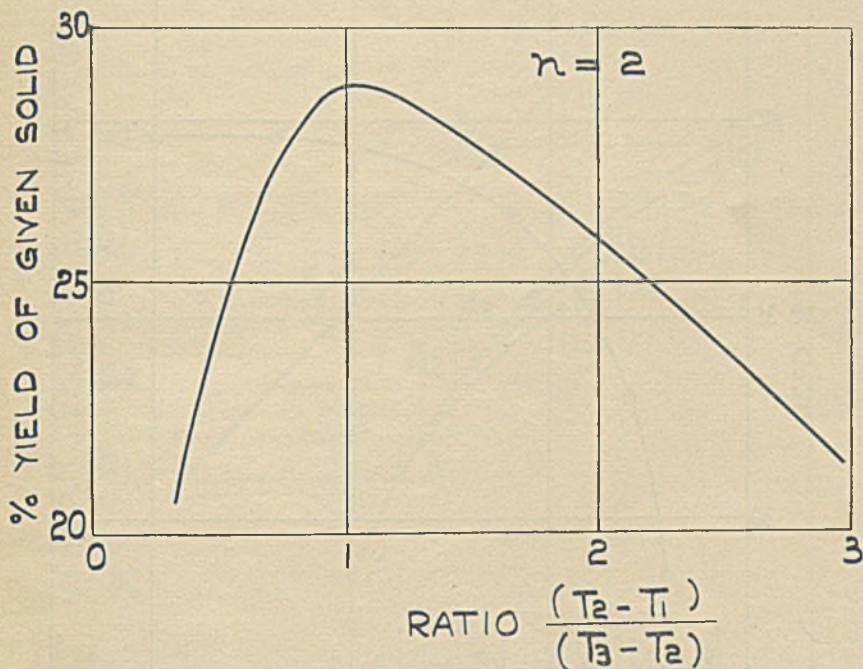


FIG. 7.

the second-stage temperature was greater than the melting range of the solid from the first stage. The temperature increment applied to the  $n$ th stage must therefore always be smaller than the melting range of the solid phase obtained from the  $(n-1)$ th stage.

In Fig. 7 the yield of a given solid obtained by some of these two-stage processes has been plotted against the ratio  $(T_2 - T_1)/(T_3 - T_2)$ , from which it will be observed that the yield is a maximum when the ratio  $(T_2 - T_1)/(T_3 - T_2) = 1$ —that is, when two stages of equal temperature increments are employed. This is a general rule, and the yield of a given solid for an  $n$ -stage process is a maximum when the stages are of equal temperature increments. This particular case is analogous to the multiple extraction of a solution with a liquid for which it has been proved that the

most efficient extraction is obtained when the solvent is subdivided into batches of equal volume.<sup>5</sup>

In Fig. 8 the yield of a solid of given composition is plotted against the number of stages  $n$  for an  $n$ -stage process, employing stages of equal temperature increments, from which it will be seen that the yield of a given solid approaches a maximum when  $n$  approaches infinity, but that this maximum yield is closely approximated in a finite number of stages—viz. 12

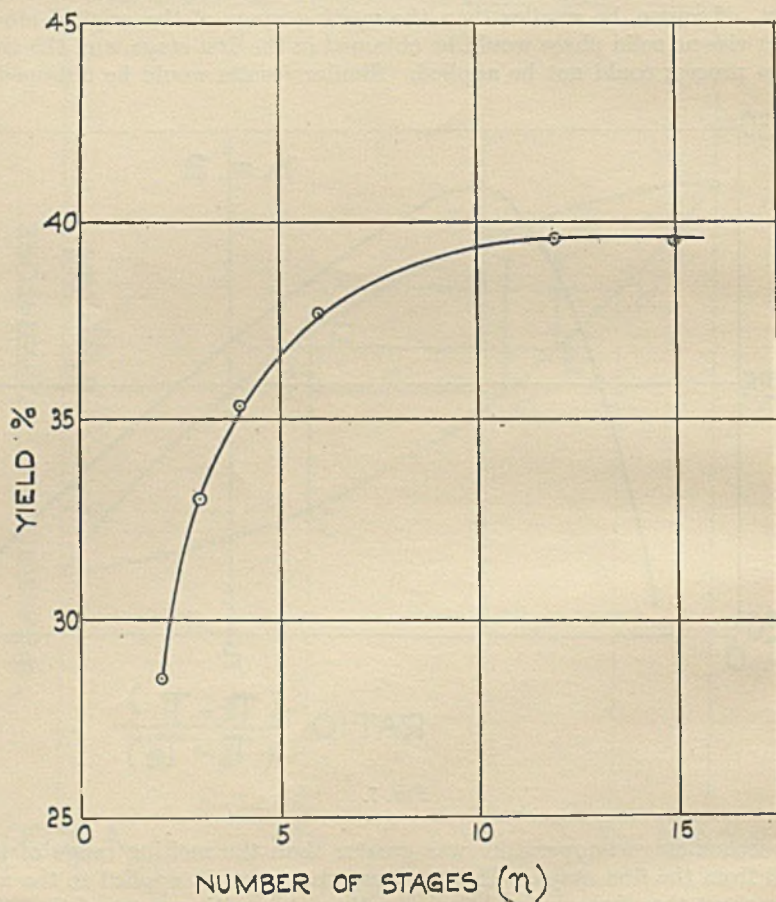


FIG. 8.

in the figure. Again an analogy exists between this and the multiple solvent extraction process, as the results obtained with a finite volume of solvent subdivided into a comparatively small finite number of batches approach those obtained with a finite volume of solvent subdivided into an infinite number of batches.<sup>6</sup>

In the "sweating" process of fractional melting, a mass of solid wax is subjected to a gradually increasing temperature over a period of some hours, with continuous removal by natural drainage of any liquid phase

formed, this operation being continued until solid wax of the required melting point remains.

If in such a "sweating" process the temperature is increased at a constant rate and the liquid phase is removed as it is formed, then this process will correspond to an infinite stage process of equal temperature increments. In actual practice, however, the complete removal of the liquid phase will not occur at the formation temperature, and, owing to such drainage lag combined with non-uniform heating, a lower yield than that from the above defined infinite stage or ideal process can be normally

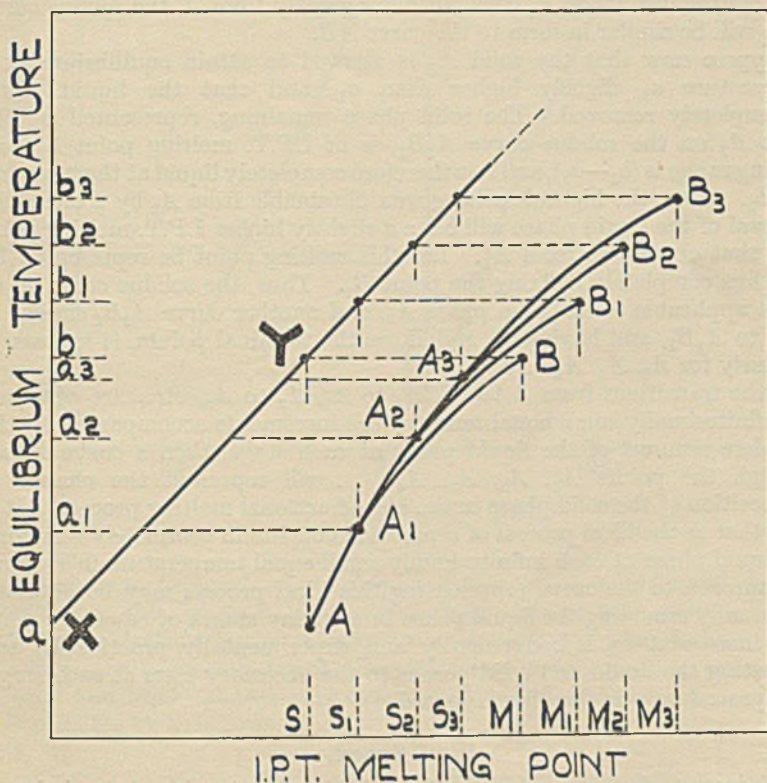


FIG. 9.

expected. An infinite stage process of equal temperature increments could therefore be used as a basis for computing sweating efficiency.

In Fig. 9  $AB$  and  $XY$  are the solidus and liquidus curves applicable to equilibrium experiments involving a one-stage removal of liquid phase from a wax stock of I.P.T. melting point  $S$  and of melting range  $(b-a)$ . The stock is completely liquid at the temperature  $b$ , and  $M$  corresponding to  $B$ , therefore represents the I.P.T. melting point of the highest-melting wax (solid phase) obtainable from this stock in a one-stage equilibrium experiment.

Suppose that the stock has attained equilibrium at a temperature  $a_1$  slightly higher than  $a$ , and that the resulting liquid phase has been completely removed from the solid. The solid phase remaining, represented by point

$A_1$  on the solidus curve  $AB$ , will have a melting point of  $S_1$ . Now this solid phase has a melting range of  $(b_1 - a_1)$ , and will be completely liquid at temperature  $b_1$ . Also, the highest-melting wax obtainable in a one-stage removal of liquid phase from the solid phase represented by  $A_1$  will have an I.P.T. melting point slightly higher than  $M$ . Let this I.P.T. melting point be represented by  $M_1$ . The point  $B_1$  is therefore defined in reference to temperature  $b_1$  and I.P.T. melting point  $M_1$ . It is now clear that the solidus curve  $AB$  will apply to the original wax stock *only* and that another curve having  $A_1$  and  $B_1$  as terminal points is necessary for the solid phase  $A_1$ . As the new stock  $A_1$  does not differ greatly from  $A$ , the solidus curve  $A_1B_1$  will be similar in form to the curve  $AB$ .

Suppose now that the solid  $A_1$  is allowed to attain equilibrium at a temperature  $a_2$  slightly higher than  $a_1$ , and that the liquid phase is completely removed. The solid phase remaining, represented by the point  $A_2$  on the solidus curve  $A_1B_1$ , is of I.P.T. melting point  $S_2$ ; its melting range is  $(b_2 - a_2)$ , and it is therefore completely liquid at the temperature  $b_2$ . Also, the highest-melting wax obtainable from  $A_2$  by a one-stage removal of the liquid phase will have a slightly higher I.P.T. melting point than that obtainable from  $A_1$ . Let this melting point be represented by  $M_2$ , thus completely defining the point  $B_2$ . Thus, the solidus curve  $A_1B_1$  is not applicable to the solid phase  $A_2$ , and another curve  $A_2B_2$  similar in form to  $A_1B_1$ , and having  $A_2$  and  $B_2$  as the terminal points, is necessary. Similarly for  $A_3, A_4, A_5, \dots$

If the transitions from  $A$  to  $A_1, A_1$  to  $A_2, A_2$  to  $A_3$ , etc., are obtained by infinitesimally small equal temperature increments accompanied by the complete removal of the liquid phase at each stage, then a curve drawn through the points  $A_1, A_2, A_3, A_4, \dots$  will represent the change in composition of the solid phase in the ideal fractional melting process. It is clear that as the ideal process of separation consists in completely removing the liquid phase at each infinitesimally small equal temperature increment, an approach to the curve representing this ideal process may be obtained by actually removing the liquid phase in as many stages of equal temperature increment as is conveniently and experimentally practicable, and subjecting the liquid and solid phases to the necessary tests at each stage. This procedure was therefore adopted.

#### WAX STOCK.

The wax stock employed in the following work was a blend consisting of equal weights of four completely refined Iranian waxes of the following I.P.T. melting points:  $130.95^\circ, 127.85^\circ, 119.85^\circ$ , and  $108.35^\circ$  F. The resulting blend was of I.P.T. melting point  $122.1^\circ$  F.

#### CONSTRUCTION OF THE FRACTIONAL MELTING-PROCESS DIAGRAM.

Two series of experiments are necessary for the construction of the required diagram:—

- (a) the determination of the solid/liquid curves representing a one-stage melting process, and
- (b) the determination of the solid/liquid curves representing a multi-stage melting process. Actually a 14-stage process was employed, as has been shown in Fig. 8, the results from a twelve stage

process approach closely to those obtained from an infinite stage process for two substances giving an equilibrium diagram of the continuous solid solution type.

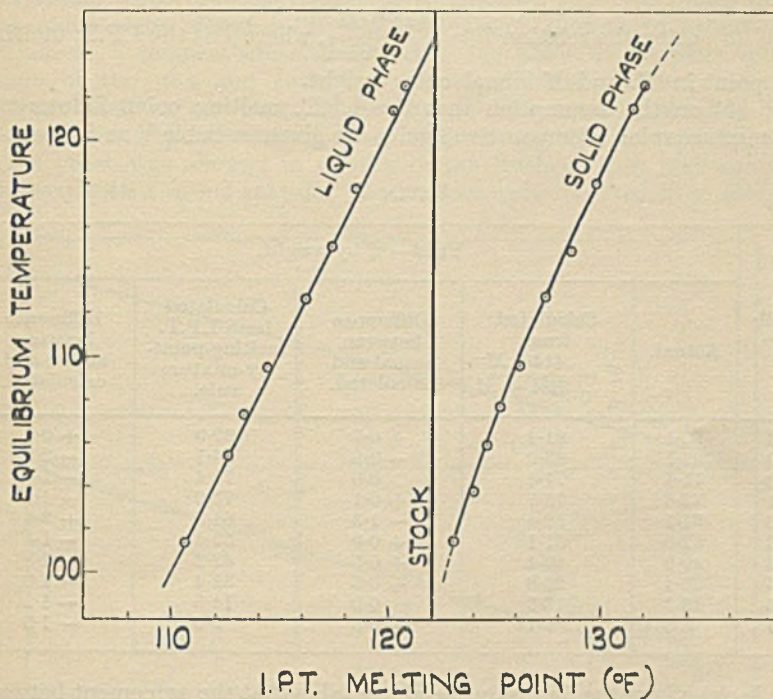


FIG. 10.

(a) *One-stage Removal of the Liquid Phase.*—The solid/liquid curves representing this process were determined at various temperatures covering the melting range of the wax stock using the procedure already described. In each experiment the yields and I.P.T. melting points of the solid and liquid phases were determined, and the relevant figures are given in Table IV as follows:—

TABLE IV.

Expt. No.	Equilm. temp. ° F.	% by weight.		I.P.T. melting point.	
		Solid phase.	Liquid phase.	Solid phase, ° F.	Liquid phase, ° F.
8	110.8	92.1	7.9	123.1	110.6
9	112.8	82.1	17.9	123.9	112.55
10	113.0	77.4	22.6	124.7	112.65
11	113.8	72.8	27.2	125.15	113.45
12	114.9	61.1	38.9	126.25	114.55
13	116.4	52.0	48.0	127.3	116.15
14	117.6	40.9	59.1	128.6	117.35
15	119.0	30.4	69.6	129.65	118.65
16	120.8	13.3	86.7	131.55	120.5
17	121.4	8.6	91.4	131.95	121.05

The results are shown graphically in Fig. 10.

The yield of solid phase was calculated from the I.P.T. melting points of the solid and liquid phases obtained in each experiment:—

(a) using the relation  $T = \frac{414.5 M}{M + 94.4}$ , where  $T$  is the I.P.T. melting point in °F. and  $M$  is molecular weight.

(b) on the assumption that the I.P.T. melting point follows the mixture rule. Comparative figures are given in Table V as follows:—

TABLE V.

Expt. No.	Yield—% by weight.				
	Actual.	Calculated from $T = \frac{414.5 M}{94.4 + M}$	Difference between actual and calculated.	Calculated from I.P.T. melting-point-by-mixture rule.	Difference between actual and calculated.
8	92.1	91.4	+ 0.7	92.0	+ 0.1
9	82.1	83.0	— 0.9	84.1	— 2.0
10	77.4	77.4	0.0	78.4	— 1.0
11	72.8	72.7	+ 0.1	73.9	— 1.1
12	61.1	62.4	— 1.3	64.5	— 3.4
13	52.0	51.1	+ 0.9	53.4	— 1.4
14	40.9	40.4	+ 0.5	42.2	— 1.3
15	30.4	29.8	+ 0.6	31.4	— 1.0
16	13.3	13.3	0.0	14.5	— 1.2
17	8.6	9.1	— 0.5	9.6	— 1.0

It is clear from the figures in the above table that the agreement between the actual and calculated yields is closer when the relation  $T = \frac{414.5 M}{94.4 + M}$  instead of the simple mixture rule is used for the calculation of the latter.

The yield/melting point graph for the two phases is given in Fig. 11, from which it is seen that the yield is a linear function of the I.P.T. melting point. For yields of the liquid phase lower than 10 per cent. the I.P.T. melting point is slightly lower than indicated by the linear relationship, and it is suggested that this may be due to the presence in the wax stock, of a small amount of oil, probably contained initially in the wax of I.P.T. melting point 108.35° F., the lowest melting of the four commercial waxes comprising the stock. Assume, for example, that the original 108.35° F. I.P.T. melting point wax contains 1 per cent. oil. The oil content of the wax stock, which contains 25 per cent. of this particular wax, is therefore 0.25 per cent. Now, it is likely that whatever the yield of liquid phase, most of the oil would be present in this phase, due to the press method employed for the separation of the phases. Thus, liquid phase obtained from an experiment in 5 per cent. yield would contain approximately 5 per cent. oil. By comparison with data obtained in determinations made to study the effect of the addition of oil on the I.P.T. melting point of a wax, it was concluded that the presence of this amount of oil would explain this deviation from the linear relation. With higher yields of liquid phase,

the oil/wax ratio decreases and the effect of the oil on the I.P.T. melting point becomes less pronounced until at 20 per cent. yield it is negligible, and the linear relationship then holds.

(b) *Multi-stage (14-stage) Removal of Liquid Phase.*—98 grams of the wax stock were placed in the apparatus and allowed to attain equilibrium at a temperature slightly above the point of complete solidification of the wax and such that the equilibrium mixture contained approximately 5 per cent. liquid phase. After equilibrium had been attained the experiment was completed as described previously. The liquid phase was allowed to solidify in the Buchner flask and was then removed with a nickel spatula. Last traces were removed from the flask

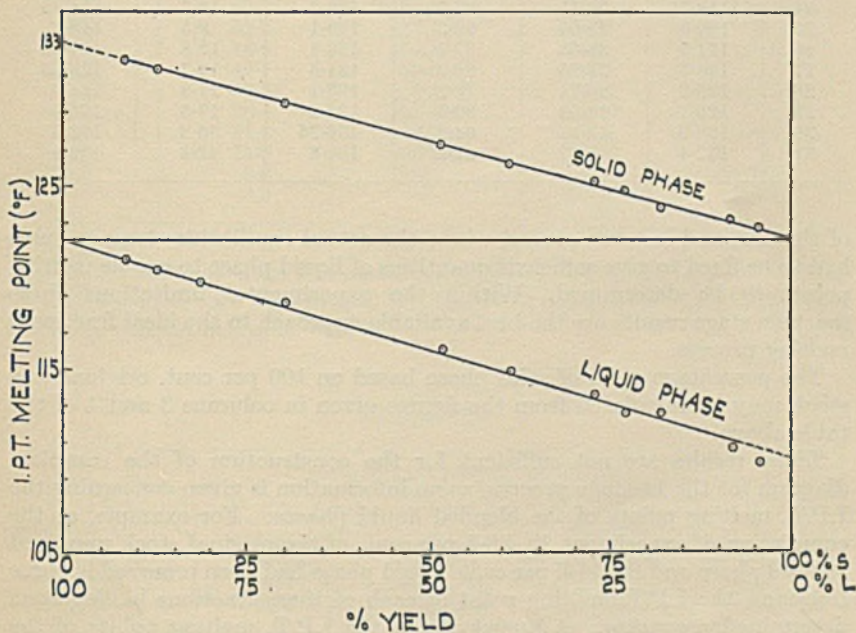


FIG. 11.

with petroleum ether; the solvent was evaporated and the traces of wax remaining were added to the bulk of the liquid phase. The solid phase was removed from the apparatus, weighed, its melting point determined, liquefied, and replaced in the apparatus. The thermostat was then set at a slightly higher temperature, such that approximately 10 per cent. liquid was present in the equilibrium mixture. After reaching equilibrium, the solid and liquid phases were separated in the usual manner and treated as described above. This procedure was repeated employing as nearly as possible equal temperature increments, until the quantity of solid remaining became so small that it was impossible to continue further. In all, fourteen separations were made. Essential figures for each of the fourteen experiments are given in Table VI. As far as possible equal temperature increments were employed in each succeeding stage, with the exception



TABLE VI.

Expt. No.	Equilm. temp. ° F.	Wt. solid phase taken gms.	Solid phase.		Liquid phase.	
			Wt. %.	I.P.T. melting point, ° F.	Wt. %.	I.P.T. melting point, ° F.
18	110.2	97.95	95.6	122.75	4.4	109.85
19	111.0	92.27	97.4	123.05	2.6	—
20	112.7	83.68	94.9	123.5	5.1	112.55
21	114.1	82.23	87.0	124.85	13.0	113.85
22	115.8	70.42	87.8	126.05	12.2	115.5
23	117.1	60.58	89.9	126.95	10.1	116.9
24	118.7	52.11	87.7	128.2	12.3	118.45
25	120.0	43.66	90.5	129.1	9.5	119.7
26	121.5	38.68	87.2	130.1	12.8	121.25
27	123.5	32.85	80.3	131.5	19.7	123.25
28	125.2	25.71	78.2	133.1	21.8	124.9
29	126.7	17.53	82.5	134.2	17.5	126.5
30	128.9	13.87	64.2	136.35	35.8	128.6
31	132.4	8.67	57.2	138.6	42.8	132.1

of the first and last two stages, where the actual equilibrium temperatures had to be fixed to give sufficient quantities of liquid phase to enable melting points to be determined. Within the experimental limitations these fourteen stage results are the best available approach to the ideal fractional melting process.

The percentage yield of solid phase based on 100 per cent. original wax stock may be calculated from the figures given in columns 3 and 4 of the table above.

These results are not sufficient for the construction of the complete diagram for the 14-stage process, as no information is given concerning the I.P.T. melting points of the blended liquid phases. For example, at the completion of experiment 20, 88.4 per cent. of the original stock remained as solid phase and the 11.6 per cent. liquid phase had been removed in three fractions, the I.P.T. melting point of each of these fractions having been determined *separately*. A knowledge of the I.P.T. melting points of the blended liquid fractions is desirable, and the fractions were therefore re-blended in their equivalent amounts and the I.P.T. melting point of each blend determined. Results are appended in Column 5 of Table VII (p. 447), in which are also recorded the yield of the solid and liquid phases as percentages of the stock.

The I.P.T. melting point of the 100 per cent. blended liquid phase should, of course, be 122.1° F.—that of the original wax stock—and considering the number of steps involved in its determination, the actual figure of 121.95° F. obtained for the re-blended stock is very satisfactory.

As the yields of both phases and the I.P.T. melting point of the solid phase are known, the I.P.T. melting points of the various blended liquid phases may be calculated by applying the relation  $T = \frac{414.5 M}{94.4 + M}$ . As a further test of the applicability of this relation, the yields of the phases were calculated in this manner from the known I.P.T. melting points.

TABLE VII.

Expt. No.	Solid phase.		Blended liquid phase.	
	Yield wt. % on stock.	I.P.T. melting point, °F.	Yield wt. % on stock.	I.P.T. melting point, °F.
—	100.0	122.1	0.0	—
18	95.6	122.75	4.4	109.85
19	93.1	123.05	6.9	110.25
20	88.4	123.5	11.6	—
21	76.9	124.85	23.1	112.55
22	67.5	126.05	32.5	—
23	60.7	126.95	39.3	114.05
24	53.3	128.1	46.7	—
25	48.2	129.1	51.8	115.30
26	42.1	130.1	57.9	—
27	33.8	131.5	66.2	116.95
28	26.4	133.05	73.6	—
29	21.8	134.2	78.2	118.35
30	14.0	136.35	86.0	—
31	8.0	138.6	92.0	120.4
—	0.0	—	100.0	121.95

The yields calculated on the assumption that I.P.T. melting point follows the mixture rule are also given, and the comparative figures for the solid phases are given in Table VIII :—

TABLE VIII.

Stage. no.	Solid Phase, Yield % by Weight.				
	Actual.	Calculated from $T = \frac{414.5 M}{94.4 + M}$ .	Difference between actual and calculated.	Calculated from Melting-point-by-mixture rule.	Difference between actual and calculated.
4	76.9	76.5	+ 0.4	77.6	— 0.7
6	60.7	60.7	± 0.0	62.4	— 1.7
8	48.2	48.0	+ 0.2	49.3	— 1.1
10	33.8	34.1	— 0.3	35.4	— 1.6
12	21.8	23.3	— 1.5	23.6	— 1.8
14	8.0	8.6	— 0.6	9.3	— 1.3

It is clear from the data included in Tables V and VIII that agreement between the actual and calculated yields is closer when the relation  $T = \frac{414.5 M}{94.4 + M}$  is used for the calculation of the latter. The use of this relation is therefore justified for this wax stock, but at the same time it will be noticed that there is no very serious discrepancy between the actual and the calculated values when the latter are calculated on the assumption that the I.P.T. melting point follows the mixture rule.

## LIQUID/SOLID CURVES FOR FOURTEEN-STAGE PROCESS.

The curves plotted from the data contained in Tables VI and VII are shown in Fig. 12.

The yield/I.P.T. melting point curves for the fourteen-stage process and also the corresponding curves for the one-stage process are given in Fig. 13. Comparison of the two curves for the respective solid phases confirms the conclusion already discussed that the yield of solid of any given I.P.T. melting point, within the range possible, is higher in a multi-stage than in a one-stage process.

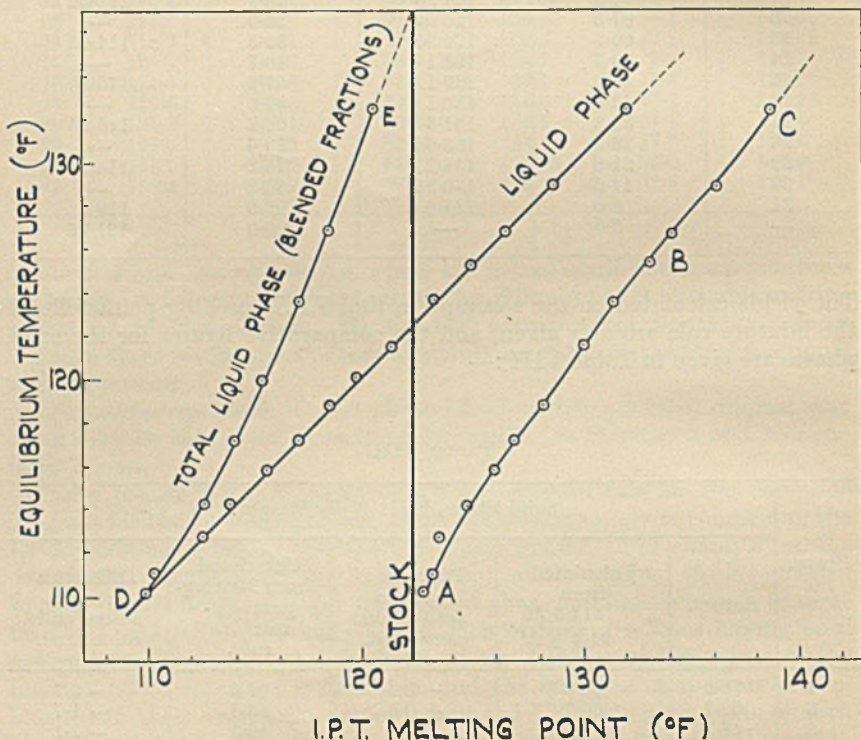


FIG. 12.

The complete diagram, which is applicable to the process both qualitatively and quantitatively, is given in Fig. 14, and is based essentially on Figs. 10 and 12, and includes the curve  $T = \frac{414.5 M}{M + 94.4}$ . This diagram will be considered sectionally.

CURVES *AB* AND *DE*.

*AB* and *DE* represent the solidus and liquidus curves applicable to a one-stage separation of the two phases at any temperature within the limits of their co-existence. *AH* is the stock line, the wax stock having an

I.P.T. melting point of  $S'$  corresponding to a calculated molecular weight of  $S''$ . The temperature  $a$  corresponding to  $A$  represents the point at which the stock just begins to melt when heated. It is completely liquid at temperature  $b$  corresponding to  $B$ , and the temperature range ( $b - a$ ) therefore represents the melting range of the stock. It is found experimentally that the liquid phase has, in general, an I.P.T. melting point of  $0.2-0.3^\circ \text{F}$ . lower than the equilibrium temperature. The liquidus curve  $DE$  may therefore be considered as a straight line only slightly removed from the  $45^\circ$  line.

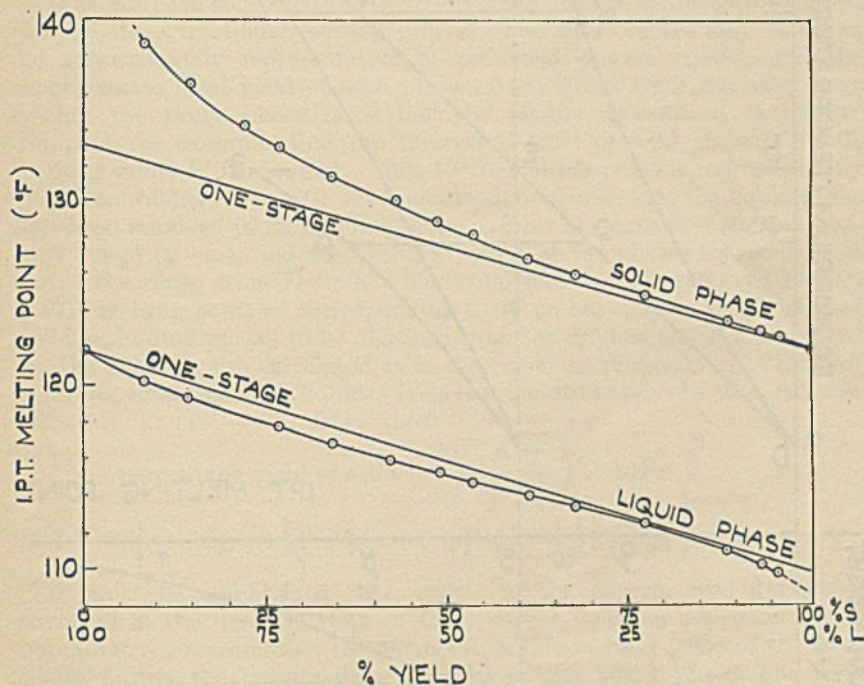


FIG. 13.

These curves may be applied quantitatively in the following manner. Suppose the stock attains equilibrium at any temperature  $x$  within its melting range, as represented by point  $S_1$ . The equilibrium mixture consists of solid and liquid phases represented respectively by the points  $P$  and  $Q$  on the solidus and liquidus curves, and having melting points of  $p'$  and  $q'$  and calculated molecular weights of  $p''$  and  $q''$  respectively. The relative amounts of solid and liquid phases at this temperature are calculated from the ratio  $(S'' - q'')/(p'' - S'')$ , from which

$$\text{percentage yield of solid phase} = \frac{(S'' - q'')}{(p'' - S'')} \times 100$$

and

$$\text{percentage yield of liquid phase} = \frac{(p'' - S'')}{(p'' - q'')} \times 100$$

CURVES *AC*, *DEF*, AND *DG*.

The curves *AC*, *DEF*, and *DG* approach the infinite-stage or ideal fractional melting process curves. Curve *AC* represents the change in I.P.T. melting point of the solid phase during fourteen small approximately

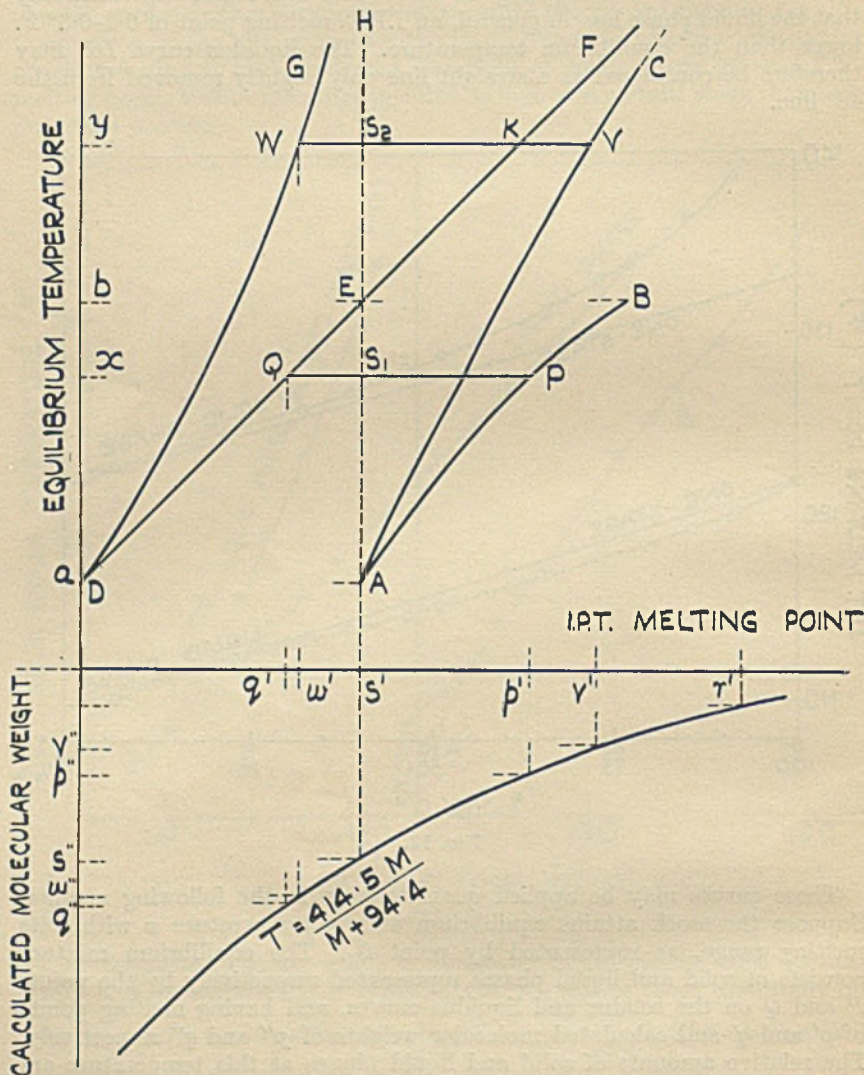


FIG. 14.

equal temperature increments, after each of which the resulting small amount of liquid phase is completely removed from the solid. It was found in the fourteen-stage experiments, as in the single-stage experiments, that the I.P.T. melting point of the liquid phase at each removal stage was, in general, 0.2–0.3° F. lower than the equilibrium temperature. The change

in I.P.T. melting point of the liquid phase is represented by  $DEF$ , where  $DEF$  may be considered, within experimental error, as a straight line. The composition of the blended liquid phases is given by the curve  $DG$ , and this curve therefore gives the I.P.T. melting point of the total blended liquid phase corresponding to any solid phase represented on  $AC$ .

It is clear that the solid phase changes in I.P.T. melting point along  $AC$ ; the total liquid phase removed changes in I.P.T. melting point along  $DG$ ; whilst the I.P.T. melting point of the liquid phase being removed at any stage of the process is given by the equivalent point on the curve  $DEF$ .

If as has been suggested this fourteen-stage process approaches the ideal infinite-stage fractional melting process, then these curves may be taken as approximately representative of the ideal process curves, and the approximate ideal yield of solid phase of any given I.P.T. melting point within the range investigated may be readily ascertained therefrom. Suppose, for example, that the theoretical yield of solid phase of I.P.T. melting point  $V'$  is required. This I.P.T. melting point is represented by  $V$  on the solidus curve  $AC$ . It is assumed, of course, that the liquid phase has been removed in an infinitely large number of stages over the temperature range  $(y - a)$ , and the melting points of the phases removed must cover the range from  $D$  to  $K$ . The total liquid phase removed has an I.P.T. melting point  $w'$  corresponding to  $W$  on curve  $DG$ . The yields of solid and liquid phases to be obtained from the original stock, represented by the point  $S_2$ , are calculated as in the one-stage removal. The ratio of solid to total blended liquids, is given quantitatively by the relation  $(S'' - W'') : (V'' - S'')$ , from which

$$\text{percentage yield of solid} = \left( \frac{S'' - W''}{V'' - S''} \right) \times 100$$

$$\text{and percentage yield of blended liquids} = \left( \frac{V'' - S''}{V'' - W''} \right) \times 100$$

It must be emphasized that, owing to the experimental difficulties involved in the determination of these curves, only an *approach* to the actual curves representing the change in I.P.T. melting point of the solid phase during the infinite-stage removal of the liquid phase, has been obtained.

The authors have to thank the staff of the Anglo-Iranean Oil Co.'s Llandarcy refinery for their help in supplying materials used in carrying out this work.

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Dept. of Oil Engineering and Refining,  
The University,  
Birmingham.

## THE HYDROGENATION OF PETROLEUM FRACTIONS, EMPLOYING A LARGE PERCENTAGE OF CATALYST.\*

By H. I. WATERMAN, Hon.M.Inst.Pet., and C. VAN VLODROP.

IN the graphical-statistical method of analysing hydrocarbon mixtures, as evolved in recent years in the laboratory for Chemical Technology at the Technical University of Delft,<sup>1</sup> it is often necessary to convert certain fractions by hydrogenation into a completely saturated hydrocarbon mixture. Not only is olefinic unsaturation, such as may occur in cracked distillates, removed in this hydrogenation<sup>2</sup> but at the same time the aromatic hydrocarbons are also converted into completely saturated products.

The process is usually carried out by heating the petroleum fraction to be examined with 10–20 per cent. by weight of nickel on kieselguhr (1 nickel: 5 kieselguhr) in rotating autoclaves with hydrogen under high pressure. The temperature used for this purpose is generally between 250° and 285° C. It has been demonstrated by special research that in normal cases only saturation of the hydrocarbons occurs.<sup>3</sup> There is no destruction, and the hydrocarbon mixture undergoes no change either in the number of rings or in the degree of branching. It is obvious that if there should be any doubt with respect to the latter, we must make sure that the hydrogenation carried out under high pressure has solely caused saturation of unsaturated constituents, so that no side reactions have taken place.

If the catalytic hydrogenation under high pressure, as described above, is applied to synthetic products, such as obtained in the polymerization of pure unsaturated hydrocarbons or as by-products in alkylation processes, the nickel catalyst usually employed will as a rule not decline rapidly in activity. The position is different, however, in the case of products containing components which cause a marked falling off in the activity of this catalyst. Various fractions obtained by the distillation of natural petroleum contain such deleterious components. Various sulphur compounds are undoubtedly to be regarded as such, and it is also advisable for other reasons, to remove such sulphur from the mixture. As a matter of fact, it is actually to be regarded as an advantage of catalytic hydrogenation with nickel, that as a result of the sulphur being bound by the catalyst the reaction products formed, if not free from sulphur, contain very little of this element. As a result, we obtain by catalytic hydrogenation under high pressure, saturated hydrocarbon mixtures which can easily and rapidly be examined by the graphical-statistical method referred to above. Furthermore, these products are completely colourless, and as far as the lower fractions are concerned, homogeneous oils; the higher fractions, though likewise completely colourless, may be solid or semi-solid owing, for instance, to paraffin wax separating out.

If, prior to hydrogenation, the sulphur contents of the oil fractions to be

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\* Paper received 12th April, 1940.

examined are very high, it should be determined in each individual case what effect this removal of sulphur has with respect to the structure of the molecular complexes deprived of their sulphur.

Wherever the activity of the catalyst is reduced by the presence of deleterious components, the number of times the catalyst has to be renewed may become so great as to hamper seriously the practical application of catalytic hydrogenation.

The authors have succeeded in eliminating this difficulty by adopting a different method, utilizing a very large quantity of catalyst.

### *Experimental Section.*

In this investigation we used a large number of fractions obtained by distillation *in vacuo* from crude oils freed from their lighter components by ordinary distillation. Below a description will be given of some experiments with fractions of a Venezuelan petroleum. These fractions will be indicated by the numbers III, IV, and V (cf. table).

Fraction IV was at first hydrogenated at a maximum temperature of about 280° C. with 10–17 per cent. by weight of nickel on kieselguhr. This catalyst contains 5 parts by weight of kieselguhr to 1 part by weight of nickel. The hydrogenation was found to proceed extremely slowly, despite the fact that for each treatment the catalyst was invariably replaced by fresh material. No less than twenty-six times was fraction IV subjected to this hydrogenation with hydrogen under high pressure. Each time the autoclave containing the oil was raised to the maximum temperature of approximately 280–285° C in about 1 hour. Thereafter there was scarcely any further drop in pressure.\* After each such hydrogenation the autoclave was cooled. Strange to relate, despite the twenty-six successive treatments, the oil fraction was far from being completely hydrogenated. In the meantime we had learnt from other experiments that this catalytic hydrogenation under high pressure could be considerably improved by using a much larger quantity of catalyst. Consequently, we now hydrogenated the oil—still incompletely hydrogenated after twenty-six treatments—a further two times with 100 per cent. by weight nickel on kieselguhr (1 nickel : 5 kieselguhr) at a maximum temperature of 300° C. with hydrogen under high pressure. It was surprising to find that the hydrogen was absorbed much more rapidly and that a completely saturated product was obtained. That this product was saturated is evident from the constants inserted in the table. The refractive index,  $n_D^{20}$ , of the product obtained after twenty-six treatments had fallen from 1.5143<sup>5</sup> to 1.5000. The specific gravity,  $d_4^{20}$ , had dropped from 0.9255 to 0.9018. The aniline point had risen from 62.2° C to 71.2° C. It will be seen from the table, however, that the complete saturation caused a further great change in the constants. The refractive index fell to 1.4778, the specific gravity to 0.8750, whilst the aniline point was about 20° C. higher than for the intermediate product obtained after the twenty-six treatments.

We would add that the specific dispersion,  $\frac{n_G - n_C}{d} \cdot 10^4$ , became 154.

\* Reduced to 0° C.



This is proof that the final product obtained could actually be regarded as completely saturated.<sup>4</sup> The aniline point read off from the graph of the aniline points for saturated hydrocarbon mixtures<sup>4</sup> was found to correspond, for the molecular weight of 303 and the specific refraction of 0.3234, with the experimentally obtained value (91° C). Further, this petroleum fraction contained an average of 2.2 rings per molecule, whilst it may be deduced from the values for the specific refraction and specific parachor that this oil has an average of four branches per molecule.

That the favourable result of the hydrogenation is really exclusively due to the large quantity of catalyst finally used was proved by the examination of two fractions, Nos. III and V (see table) obtained from the same Venezuelan petroleum. Employing each time 100 per cent. by weight of catalyst, we succeeded in completely saturating fraction III in three runs at about 280° C. (maximum temperature 290° C.). In the case of fraction V the same result was achieved after four treatments. Each treatment usually lasted 1 hr. at the operating temperature. The table also shows the constants for fractions III and V, both before and after hydrogenation. From the values given for the specific dispersion, as well as from the correlation between the aniline points read off in the graphs showing the aniline points for the respective molecular weights and specific refractions and those determined, it is once more evident that the products are completely saturated after hydrogenation. For the rest the results of the analyses for the fractions III, IV, and V, both before and after hydrogenation, are analogous.

In connection with this investigation the question arose, to what extent the use of the large quantity of catalyst would involve a risk of the products examined decomposing or changing their structure, since the large quantity of catalyst alters completely the consistency of the mixture of oil and catalyst. The product acquires the properties of a powder greasy to the touch, both before and after hydrogenation. In view of this fact we might expect, or at any rate we must take into account, the possibility of the product burning or becoming overheated. It has been proved experimentally, however, that in an analogous case this danger is non-existent. This was proved in the case of fraction V of another Venezuelan oil. The latter was hydrogenated by the old method. A thirteen-fold treatment was required, whilst when working with the large quantity of catalyst the completely saturated product was obtained after three treatments. It may be added that in the latter case the product was practically saturated after only two treatments. The physical constants showed the two products to be practically identical. It is to be expected, therefore, that in such cases the treatment with the large quantity of nickel catalyst will not give rise to decomposition processes or changes in structure.

By the above method it is also possible to convert asphaltic residues into mixtures of saturated hydrocarbons, the yields being good.

It is remarkable that the hydrogenation is so greatly accelerated by the use of the very large quantity of catalyst. It stands to reason that this result is important for hydrocarbon research. It is to be expected that in certain cases it will also be of technical significance. In this connection we have in mind those cases where the use of sulphur-resisting and poison-resisting catalysts in general is impossible. If it is possible to use these

poison-resisting catalysts at low temperature, it is unnecessary to adopt the above new method employing the very large quantity of catalyst.

In conclusion we should like to express our thanks to Mr. J. van Wijk, who carried out a considerable share of the experimental work.

### Summary.

In the examination of hydrocarbon mixtures it is frequently necessary to saturate these mixtures completely by hydrogenation. If the hydrogenation is effected with a nickel catalyst, it is in many cases necessary with technical oil fractions to repeat the hydrogenation treatment many times, employing a fresh quantity of catalyst for each treatment.

#### Fractions from Venezuelan Petroleum.\*

	Fraction III.	Fraction III hydrogenated.	Fraction IV.	Fraction IV hydrogenated.	Fraction V.	Fraction V hydrogenated.
Molecular weight . . . . .	248	255	304	303	353	351
$n_D^{20}$ . . . . .	1.4978	1.4689	1.5104	1.4753	1.5187	1.4817
$n_D^{20}$ . . . . .	1.5013	1.4712	1.5143	1.4778	1.5227	1.4843
$n_p^{20}$ . . . . .	1.5099 ?	1.4771	—	1.4839	—	1.4906
$n_D^{20}$ . . . . .	—	1.4820	—	1.4888	—	1.4956
$d^{20/4}$ . . . . .	0.9036	0.8635	0.9255	0.8750	0.9396	0.8880
$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$ . . . . .	0.3262	0.3238	0.3254	0.3234	0.3250	0.3224
(0; 20° C.)						
$(n_G - n_O) \cdot 10^4$ . . . . .	—	131½	—	135	—	138
$\frac{n_G - n_O}{d} \cdot 10^4$ . . . . .	—	152	—	154	—	155½
Aniline point :						
Determined, ° C. . . . .	58.1	83.5	62.2	91.1	67.0	97.3
Read off from the graph for saturated hydrocarbons, ° C. . . . .	—	82	—	91	—	97½
$\sigma^{20}$ in dynes/cm. . . . .	30.91	29.79	31.97	30.60	32.58	31.55
$\frac{\sigma^{1/4}}{d}$ (20° C.) . . . . .	2.609	2.706	2.569	2.688	2.543	2.669
Average number of rings from specific refraction :						
Per molecule . . . . .	—	1.9 <sup>s</sup>	—	2.2	—	2.6
Per molecular weight 100 . . . . .	—	0.7 <sup>s</sup>	—	0.7	—	0.7 <sup>s</sup>
Average number of rings from specific parachor :						
Per molecule . . . . .	—	2.1 <sup>s</sup>	—	2.6	—	3.1
Per molecular weight 100 . . . . .	—	0.8 <sup>s</sup>	—	0.8 <sup>s</sup>	—	0.9
Average number of additional branches :						
Per molecule . . . . .	—	2	—	4	—	5
Per molecular weight 100 . . . . .	—	1	—	1 to 2	—	1 to 2

\* Collection Chemical Technology tin No. 8.

We have now succeeded in considerably accelerating the catalytic hydrogenation under high pressure by using a very large quantity of catalyst (100 per cent. and more). The oil fractions examined showed no decomposition nor objectionable changes in structure. We thus succeeded in converting dark and even asphaltic oil fractions or residues into completely colourless saturated products by subjecting them a certain number of times to hydrogenation by the new method.

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- <sup>4</sup> *Ibid.*, 1935, 21, 661, 701.

*Laboratory for Chemical Technology,  
The University,  
Delft.*

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## Geology and Development.

**1231.\* Results to Date of Drilling for Oil in England and Scotland.** W. Kauenhowen. *Oel u. Kohle*, 15.3.40, 36 (11), 99-109.—Prospecting licences issued between December 1935 and September 1939 closely cover the various oil provinces, amount to about one-eighth of the total area of the country, and are divided among four companies: D'Arcy Exploration Co. (64%), Anglo-American Oil Co. (21%), Gulf Oil Co. (Great Britain) (13%), and Steel Bros. (2%).

From the geological point of view, three oil provinces can be distinguished: the Carboniferous, the Zechstein, and the Mesozoic (Jurassic and Wealdon).

The oil shows and the results of drilling in the South of England Mesozoic area are described. The explanation for the failure of the borings in this area may be sought in the palæogeographical and tectonic conditions. These are discussed, and it is concluded that this failure is due to the lack of suitable reservoir rocks, the lack of "salt tectonics," and the small subsidence of the basin of sedimentation as compared with conditions in North-west Germany.

The Zechstein oil province is limited to the extreme east of England and is small in extent. Its development is very similar to the German Zechstein, but the oil shows are unimportant, and are confined in the main to bituminous odours in the mid Zechstein and to rare traces of liquid oil. Anticlines in the Yorkshire Jurassic are being tested for the Thuringian types of deposit.

Oil shows are more frequent and important in the British Carboniferous. These are described, as are also the results of the earlier drilling in the Midlands. After the failure of the Gun Hill and Edale wells, drilled during the present period, attention was turned to buried Carboniferous structures such as the Derby and Notts. coal-fields. A subsidiary anticline on the easterly plunge of this basin, in the neighbourhood of Eakring, was drilled and gave an initial production of 17 tons/day from a 45-ft. sandstone in the Lower Coal Measures. On the west side of the Pennines, where the Lancashire Coal Basin plunges westwards under a Permo-Triassic cover, seven out of eleven wells at Formby found Keuper Marl impregnated with light oil at depths of 100-120 ft. 70 tons of oil were obtained from three wells in 1½ months. This is undoubtedly a secondary deposit, and demands closer attention, which, because of the complicated conditions due to faulting and glaciation, will involve more drilling and geophysical work.

Conditions are different in Scotland, where oil-impregnated sandstones are interbedded in the oil-shale series. It seems probable that the greater part of the Scotch oil is not normal crude, but is derived from contact metamorphism of the shales. The most important structure there is the d'Arcy-Cousland anticline. A small oil production is obtained, but the hope of finding lower sands has not materialized. Prospecting north of the Forth led to the discovery of an anticlinal structure at Kirkaldy, but deep drilling on this had not commenced at the outbreak of war.

S. E. C.

**1232.\* Greek Exploration.** R. G. Drown. *World Petrol.*, Feb. 1940, 11 (2), 23.—The first wildcat drilled by Hellen in Greece is near the Ionian sea-coast, on the west side of the Peloponnesian peninsula, 15 ml. from Pyrogos. It is within sight of the island of Zante. In addition to favourable geological structure, there are numerous surface indications of oil and gas.

Oil manifestations in Greece are mainly in Miocene beds. In the test-well oil showings were found more than 4000 ft. deep, and the same area has given a gas yield said to amount to 20,000,000 cu.ft./day.

G. D. H.

**1233.\* Petroleum Exploration in Brazil.** Anon. *World Petrol.*, Feb. 1940, 11 (2), 26.—In the past 20 years sixty-four wells have been drilled in Brazil in search of oil. The most favourable areas for oil are believed to be the Atlantic coast sedimentary belt from the State of Rio Grande do Norte to the State of Rio de Janeiro, Western Acre near the frontier of Peru, and the Permo-Triassic belt of Southern Brazil. On the Atlantic coast are folded and faulted Cretaceous and Tertiary beds, with traces of oil in the Cretaceous. In 1939 a well penetrated a Cretaceous oil horizon at 702 ft.

The centre of the Acro region is mainly Tertiary, and there are also beds corresponding to the petroliferous horizon at Aguas Calientes in Peru.

In the Bahia Reconeavo are Cretaceous sandstones and bituminous shales.

G. D. H.

**1234.\* Nebraska Joins the Oil States.** J. A. Kornfeld. *World Petrol.*, Jan. 1940, 11 (1), 33.—Commercial oil production was first obtained in Nebraska in November 1939, when a wildcat in the south-east found oil in a Silurian limestone. The discovery can be attributed to the reflection seismograph. This well topped the Mississippian limestone at 2029 ft. and Silurian limestone at 2288 ft. In the first day's pumping 130 bbl. of oil were produced.

Glacial deposits are at the surface in this area, resting on Permian and Pennsylvanian. Immediately under the Mississippian are Silurian dolomites. The greatest thickness of Silurian recorded is 459 ft. Ordovician and Cambro-Ordovician are known to be present, and wells have penetrated pre-Cambrian schist. The nearest Silurian outcrop is 235 ml. due east, whilst the nearest Silurian production is 170 ml. to the south-west in Kansas, where accumulation is the result of pinching out of the Hunton on the flank of the Graber structure. 250 ml. to the east is the old Colmar field of Illinois.

The local structure of the Falls City field is a secondary fold to the east of the Table Rock anticline, itself the northern extension of the Nemaha Granite Ridge. The structure may be faulted.

G. D. H.

**1235.\* Geology and Economic Significance of Mississippi Oil Development.** J. A. Kornfeld. *World Petrol.*, March 1940, 11 (3), 38.—The Tinsley field is in the west central part of the State. It has eleven wells proving an area of 1200 acres, and its daily production is 2100 bbl. Its discovery led to great exploratory activity in Mississippi. Semi-commercial production was found at Jackson in 1930 in the Selma Chalk. In 1932 dead oil was discovered in the Eutaw, near Quitman.

Tinsley, opened in 1939, yields oil from the Woodruff sand of the Selma Chalk at over 4500 ft. There is a southerly plunging anticline, apparently a truncated structure of igneous origin, with no free gas, and a sand of variable thickness. The structure was first indicated geologically and then checked geophysically.

In January there were sixty-five geophysical parties at work in Mississippi—thirty seismic, thirty gravity, and four magnetic (in igneous province of Western Mississippi).

Various wells have reached igneous rocks in Western Mississippi. Some of these are post-early Cretaceous. At Jackson there are igneous rocks.

The Jackson gas-field covers 7500 acres. It was discovered in 1930 at a depth of 2430 ft. in the Gulf Cretaceous. Some 84,816,231,000 cu. ft. of gas have been recovered. Some of the wells had an oil spray.

Unsuccessful attempts have been made to obtain oil and gas production on the broad, gentle Hatchotigbee anticline. In North-east Mississippi, on the south-west end of the Cincinnatti arch, the Mississippian gives gas at Amory (Hartselle and Bethel sands). Tests should be made in the Ordovician of North-east Mississippi.

G. D. H.

**1236.\* World Crude Production up 5.59%.** Anon. *World Petrol.*, Feb. 1940, 11 (2), 41.—World production at 2,076,852,000 bbl. for 1939 was 110,265,000 bbl. above the 1938 figure. U.S.A. production increased by 4.3% and that of the rest of the world by 7.6%. U.S.A. still provides more than 60% of the total oil output. Consumption seems to be increasing more rapidly outside U.S.A. than within.

Illinois had a spectacular rise to fifth place amongst the U.S.A. states.

Russia is still second on the world list of producing countries, and Venezuela third. There was a decline of 4.9% in the Rumanian production, whilst the total German output rose by 21.5%. Saudi Arabia, Canada, Egypt, and Albania had marked increases in oil production.

G. D. H.

**1237.\* Production of Oil in Western Asia.** Anon. *Rev. Pétrolif.*, 24.4.40 (883), 236.—The region between the Caucasus and the Indian Ocean yields 46,264,000 tonnes of oil/year. In 1939 Iran gave 10,367,000 tonnes, and is capable of tripling its output. Arabia's production was 525,000 tonnes and Bahrein's more than 1,000,000 tonnes.

Since 1936 Iraq has averaged more than 4,000,000 tonnes/year. Egypt gave 636,000 tonnes in 1939 and the Caucasus 29,562,000 tonnes. The aggregate is 15.6% of the world's output.  
G. D. H.

**1238.\* New Stage in the Search for Oil by the A.G.I.P.—1940-1945.** C. Migliorini. *Rev. Pétrolif.*, 27.4.40 (884), 255.—The first stage of the search for oil in Italy ended in 1933, and although the results were unimportant commercially, the data obtained were of value in directing further work. It was shown that oil possibilities existed in the Padana valley, and that there were hydrocarbons throughout the Apennines, and especially on the Adriatic side. In the second stage the adoption of rotary drilling presented some difficulties. The geological problems were still far from completely solved, but this period was marked by the definition of gas-bearing beds at Podesano and Bellena, and a small oil and gas horizon at Tramutola Potenza. Certain geological generalizations became clear, and the problems of the now stage of investigation are now well defined.  
G. D. H.

**1239.\* Oil Struck at Saint-Marcel.** G. Diehter. *Rev. Pétrolif.*, 4.5.40 (885), 267.—The Pinat well on the Saint-Marcel anticline, which found a large volume of gas in July 1939 at 1520 m., has now struck oil. Several oil-bearing beds were met, and that which is producing lies 1800-2000 m. deep. Several tonnes per hour have been produced under a pressure of 95 kg./cm.<sup>2</sup>. The oil yields 22% of gasoline, a lubricating oil comparable to Pennsylvanian bright stock, and 4% of paraffin.  
G. D. H.

**1240.\* Oil in France.** Anon. *Rev. Pétrolif.*, 4.5.40 (885), 268.—Most of the Languedoc oil indications lie near the south-east margin of the Montagne-Noire. Near Gabian is an oil seep accompanied by carbon dioxide and hydrogen sulphide. During the latter part of the nineteenth century wells and shafts were put down in this area, and in 1924 a well on an anticline gave an oil flow from the Trias at a depth of 106 m. Some fifty-seven wells were sunk, of which fourteen were producers. The maximum production was 6000 tonnes during 1926. Gabian appears to be the remnant of a petroliferous area which was largely destroyed by earth movements and igneous activity.

In 1938 a well at Pic Saint-Loup was in hard Domerian limestone at 383 m., and lay between two lines of seeps. A well drilled on Saint-Marcel anticline after geophysical work found oil impregnation at 800 m. It was stopped in black Posydonomia marls below dolomites.

At Gornies a well went to 456 m. and found oil shows, but it was affected by strong water-flows.

A second well on the Saint-Marcel anticline found gas at 1520-1530 m., which seemed wet. It was estimated to give 200,000 cu. m. of gas/day. This area has many oil shows on Cretaceous anticlines and near Trias faults.  
G. D. H.

**1241.\* Drilling in First Six Months almost at 1937 Level.** L. J. Logan. *Oil Wkly*, 8.7.40, 98 (5), 12.—Completions in the first half of 1940 were almost at the 1937 level, and were 19.4% above those of the same period of 1939. 14,911 wells were completed. A table gives the details of the completions for the first six months—number of oil, gas and dry wells, and initial production of these wells by States.

Decreased drilling as compared with 1939 is the case in Arkansas, Colorado, Kentucky, Michigan, East Texas, the Corpus Christi, and San Antonio areas of South-west Texas, and the Texas Gulf Coast. Completions in California, Pennsylvania, New York, and Illinois were respectively 27%, 69%, 118%, and 5% above the 1939 figures.

G. D. H.

**1242.\* Tennessee's Oil and Gas Prospects.** J. H. Overstreet and H. G. Maxey. *Oil Wkly*, 8.7.40, 98 (5), 35.—Oil was first produced in Tennessee 120 years ago, but few attempts have been made to develop areas in this State scientifically. East Tennessee is considered the least favourable part of the State for oil and gas, on account of its geological complexity. Oil and gas have been found in the northern part of the Cumberland Plateau in the Mississippian at shallow depths. The Highland Rim (flanks of the Nashville dome) yields oil from Mississippian-Lower Ordovician rocks at

shallow depths. There are minor flexures, and a number of fields have been developed. On the whole the wells are not large. Generally in the Highland Rim region wells located on closed structures, according to approved methods, prove profitable.

The problems associated with drilling wells in the above regions are described.

The Central Basin has mainly dense Lower and Middle Ordovician limestones at the surface, and no oil or gas has been found there. A sandy dolomitic horizon 1200-1500 ft. below the Chattanooga has a few oil and gas shows. In Western Tennessee the Palaeozoic rocks dip west very gently beneath Upper Cretaceous and Tertiary sands and gravels. More than a score of wells have reached the Palaeozoic, some having oil and gas shows in the Upper Cretaceous and also in the Palaeozoic. Geophysical work has been carried out in Western Tennessee, and two wells were drilled in areas where the nature of the structure was doubtful. One of the wells had oil shows, and geologists believe that better-placed wells will have good prospects.

G. D. H.

**1243.\* U.S. Continues to Find many New Fields.** Z. H. Mischka. *Oil Wkly*, 15.7.40, 98 (6), 15.—During the first half of 1940 about 135 new oil-fields were discovered, and new pay horizons were found at the 1939 rate. Texas has contributed the greatest number of discoveries, there being twenty-four new fields and twenty-eight new pay horizons in the south. Wilcox production was found at 8150 ft., some 150 ml. west of the nearest producer from the same zone in South Texas. In North Texas prolific wells were completed in the Bend horizon at Bonita and Ringgold. The Ellenburger dolomite was found to be productive in the K-M-A field. Four distillate fields were opened on the Texas Gulf coast, and there were eleven oil and two gas strikes in West Texas.

Thirteen oil-fields were opened in Illinois. The principal factor in Illinois production is the Lake Centralia-Salem field. Wildcatting is expected to increase in the northern part of the State. Nine wildcat oil strikes were recorded in Michigan. The Pickens field of Mississippi, a new discovery, now has four wells producing from the Midway at 4800-4900 ft. Ten new fields were opened in Louisiana, and there were two strikes in Arkansas. The main developments in California were the discovery of new deep horizons in proven areas. Oklahoma has twenty new fields, mainly small, and Kansas twelve new fields and ten new horizons in old fields. No new fields were found in the Rocky Mountain district, but there were extensions to old fields in addition to the opening of new producing zones.

The Forest City basin of Kansas, Nebraska, and Missouri has come into the limelight with two producing wells.

G. D. H.

**1244.\* Centralia Devonian Hits Peak ; Decline already Started.** H. F. Simons. *Oil Gas J.*, 11.7.40, 39 (9), 28.—In consequence of the completion of prolific Devonian wells at the northern end of the Centralia field, this field is now the third largest producing area in U.S.A. However, the decline seems to have set in already. In the week ending 29th June 119,000 brl./day came from the Devonian lime and about 5000 brl./day from the Benoist. Quite a number of wells come in at more than 10,000 brl./day.

The Devonian production seems to cover about the same area as the Benoist. About half the area is densely drilled, but the northern end has a 20-acre spacing. Nearly all the wells make water—1-80%, with an average of 5%. There is a good water drive, which is not, however, being used to the best advantage. Water encroachment has not yet caused any serious concern.

Wells decline rapidly down to about 100 brl./day—many wells fall to 10% of their initial production in 10 days. They probably give two-thirds of their ultimate production in the first two months.

No new Trenton tests have followed the Trenton discovery at Centralia.

About 10,000-12,000 brl. of oil/day come from the old Illinois fields; 10,550 brl./day from the new Indiana fields, and 13,500 brl./day from Kentucky (mainly from the old fields).

G. D. H.

**1245.\* Coming Months may be Texas' Most Active.** R. M. Sanford. *Oil Gas J.*, 11.7.40, 39 (9), 32.—Wildcatting still continues very actively in the counties bordering



the Fort Worth basin. The Hull-Silk field is proving its importance, having 295 wells producing from five horizons and not yet being fully defined. Ellenburger production has been found at 4400 ft. in K.M.A.

The older fields of North Texas, Johnson to Burkburnett, Petrolia and Nocona, are related to the Red River uplift. Almost all over Archer county are shallow fields associated with stratigraphic conditions at the northern end of the Bend Arch. The Muenster Arch or buried mountain range of the Fort Worth basin gives fields in Cooke County. These fields paved the way to the discovery of deeper fields in traps which were merely depth intensifications of the shallow producing structures.

Since the discovery of five new fields at deeper levels on the north-west rim of the Fort Worth basin, exploration has spread eastwards into Montague county.

The Walnut Bend field has thirty-five deep wells and is still expanding.

G. D. H.

**1246.\* Hungary.** Anon. *Oil Gas J.*, 11.7.40, 39 (9), 39.—Another producing field is reported to have been discovered in Hungary. It lies in the region of Szentes between the Tisza and Maros rivers, and is said to be capable of large production.

The Budafa-Pusztá field is Hungary's chief source of oil, having given 2000-4000 brl./day during 1939.

G. D. H.

**1247.\* Carboniferous Tertiary Deposits in the Southern Argentine and Chile.** J. R. Guinazu. *Bol. Inform. Petroleras*, March 1940, XVII (187), 16-71.—This is a long and very interesting article written in view of the European War, which threatens to deprive the Argentine of a regular supply of coal. Up to date no coal deposits of any importance have been discovered in the Argentine, but lignite is found in Patagonia. There is also a small lignite deposit at Cushamen. These deposits would only be of service to the Patagonian railways, as the cost of transport to Buenos Aires would be very high. There are, however, further possibilities in Patagonia and in Tierra del Fuego which should be explored at all costs. It is suggested that a Commission be appointed to study the whole question, in respect to which Sr. Guinazu's paper provides a valuable contribution.

H. I. L.

**1248. Recent Progress in Petroleum Development and Production.** H. C. Miller and G. B. Shea. U.S. Bur. Mines Reprint, 1940.—This report was first presented before a sub-committee formed to promote the conservation of petroleum in the United States; to provide for co-operation with the States in preventing the waste of petroleum; to create an office of petroleum conservation; and for other purposes. It reflects progress made in petroleum production during the five years 1934-1938 inclusive. The significant conclusion is reached that the overwhelming trend in the industry is towards the application of science and engineering to problems of exploration, drilling, and producing. During the five years under review 752 new oil-pools were discovered in the U.S.A., of which it is estimated 489 will ultimately produce more than 1,000,000 brls. of oil. Advances in exploration technique are evident from the fact that the number of major oil-fields found by scientific knowledge far exceeds those discovered by wildcat drilling. Many new pools are also being discovered in areas that former exploratory methods failed to distinguish as oil-bearing.

Wells are being drilled increasingly deeper, and because of improvements in equipment and technique it is now possible to reach depths of nearly 3 miles in the same time as it was possible to drill only some 5000 ft. a few years ago.

The production branch of the industry has benefited by the results of a vast amount of research carried out in oil-company, private, and Government laboratories. This research has concerned particularly reservoir pressures and temperatures; examination of subsurface samples of oil; the work that a given volume of reservoir fluid can perform when expanded from reservoir pressure and temperature to atmospheric conditions; the problem of fluid flow through reservoir sands; the "connate" water content of oil-sands; and physical examinations of core specimens of the formations penetrated by the wells.

There is now a marked tendency in the industry towards more economic spacing of wells and an increased general recognition of the fallacy of drilling more wells in one pool than is absolutely necessary from the point of view of oil recovery.

Proration was in the first place designed to check over-production of crude oil, but it has gradually developed into a conservation measure. By proration the production of wells is curtailed and new wells are not permitted to flow "wide open," with consequent wastage of gas and reservoir energy. It has been found that pools are most efficiently operated by utilizing to the full the energy in the reservoir. If this energy is properly conserved, the natural flowing life of wells is prolonged and the need for installing pumping equipment is postponed until practically all recoverable oil has been withdrawn from the pool.

Great advantages accrue from unitization of oil-pools, and it is surprising that the practice of operating a pool as though a single owner controlled the oil and gas rights is not more universal. The chief handicap to unitization is the barrier to participation caused by "hold-out" operators, landowners, and royalty interests who for various reasons will not join in the plan. A better understanding of the advantages of unitization by both large and small operators would no doubt lead to more widespread adoption of unit operation plans.

H. B. M.

## Geophysics.

**1249.\* Reflection and Transmission Coefficients for Plane Waves in Elastic Media.** M. Muskat and M. W. Moros. *Geophys.*, 1940, 5 (2), 115-148.—There have been no complete and systematic calculations of the reflection and transmission coefficients for plane waves incident on elastic interfaces, although the equations were derived 40 years ago. Systematic tables for those coefficients for various types of interfaces should make it possible to predict the intensity of various waves created at a single interface and also, by following each of these waves, the resultant effect of a stratum as a whole. Six sets of tables are therefore given, covering the amplitudes of reflected and transmitted longitudinal and transverse waves, their intensities, and the fractions of the incident energy carried away by them. A final table gives the reflection coefficients for the incidence upon an elastic interface of transverse waves polarized normal to the plane of incidence. Most of the results are limited to angles of incidence not exceeding 30°, but as this range is of greatest interest in reflection shooting, they should cover most of the situations occurring in practice.

S. E. C.

**1250.\* Seismic Wave Energy Reflected from Various Types of Stratified Horizons.** M. Muskat and M. W. Moros. *Geophys.*, 1940, 5 (2), 149-155.—The amplitudes and intensities of waves recorded at the surface cannot be used as a basis of interpretation, since they are the resultants of multitudes of extraneous effects superimposed on the direct reflection and refraction processes occurring at the horizons being studied. At the same time, a knowledge of the reflection and refraction coefficients can provide qualitative considerations regarding the possibility of getting satisfactory records under given conditions. Twelve examples to illustrate this are worked out, using the reflection and transmission coefficients tabulated in a previous paper (see Abs. 1249).

S. E. C.

**1251.\* Computation and Mapping of Seismic Reflection Data.** M. B. Widess and N. A. Haskell. *Geophys.*, 1940, 5 (2), 156-168.—Computations based on curved paths in order to overcome the errors involved in the assumption of a straight ray path may be subject themselves to even greater errors by the assumption that velocity is a function only of depth. This is especially the case with steeply dipping strata. As, however, such a velocity relationship is frequently assumed and in certain cases is true, a dip equation based on this rule is presented. In this equation it is assumed that the reflecting horizon is plane; the effect of curvature of the surface is therefore discussed. Further, it is assumed that the seismometer spread is orientated along the direction of maximum dip of the reflecting horizon, a direction which is generally unknown. The dip has therefore to be determined from data obtained by spreads oblique to the dip direction. This may be done by calculating the dip for each spread and assuming this to be the component of true dip in that direction. A more rigorous treatment, based on time-maps, is also given.

S. E. C.

**1252.\* Change of Reflection Amplitude and Character with Geophone Depth.** H. M. Houghton. *Geophys.*, 1940, 5 (2), 169-175.—Experiments were made at four loca-

tions in Oklahoma to determine whether the depth at which a geophone is placed beneath the surface has an appreciable effect on the character and amplitude of the recorded reflections. The records obtained from geophones placed at depths varying from 10 to 240 ft. were compared with the record given by a geophone at 2 ft. The amplitude-depth relationships had a common characteristic in a rapid decrease in reflection amplitude with a moderate increase in depth. This is undoubtedly due to an increase in acoustic impedance with depth. Efforts to correlate amplitude and character of reflections with the type of material in which the geophone was placed were unsuccessful. This was also the case with an attempt to equate the motion of the geophone at depth with movement caused by waves arriving from below plus the reflection of those waves from the surface. The ratio of reflection amplitude to ground unrest remained nearly constant while the geophone was lowered, thus indicating a tendency for no great change in the signal-noise ratio if the geophone is placed in deep holes.

S. E. C.

**1253.\* Relative Gravity Measurements Using Precision Pendulum Equipment.** M. W. Gay. *Geophys.*, 1940, 5 (2), 176-191.—Special pendulums, ground from single pieces of fused quartz, were made in order to establish stations for the calibration of gravimeters. Details of the design of the pendulums, two of which are mounted in the same support and swing 180° apart in phase, are given and data tabulated in order to illustrate the precision of the measurements.

S. E. C.

**1254.\* Recent Progress in Geophysical, Geochemical, and Electrical Prospecting Methods for Petroleum.** J. B. Eby. *Petrol. Engr.*, Midyear 1940, 11 (10), 122.—In general, the magnetometer, gravity-meter, electrical prospecting, and soil analysis are now regarded as valuable reconnaissance methods. The torsion balance is a reconnaissance and detail instrument. The refraction seismograph has been used for reconnaissance and detail, but its operation is expensive, and it is much inferior to the reflection seismograph for detail work.

The main mechanical developments have been towards an increase in portability.

The U.S.A. geophysical activity is at about last year's level.

Geochemistry is being widely applied, especially in California, the Gulf Coast, and Kansas. Geochemical well-logging is receiving increased attention and achieving more success. Geochemistry has not yet been able to establish criteria to differentiate between commercial and non-commercial accumulations of oil and gas; its results are qualitative rather than quantitative.

Cuttings can be tested geochemically, and this should be done within 48 hr. They are tested for methane, butane, pentane, and higher hydrocarbons. Examples are given of geochemical well-logging, a process which does not, however, replace electrical logging or core analysis. The data are related to the presence or absence of hydrocarbons, for their influence seems to extend short distances laterally and vertically beyond the limits of production—i.e., the effective depth of the well is increased by several hundred feet, and its effective diameter by anything up to a quarter of a mile.

Electrical transients are now capable of deep penetration, and have been used where seismic reflections are difficult to obtain.

G. D. H.

## Drilling.

**1255.\* Directional Drilling, Surveying, and Polar Core Orientation.** G. L. Kothny. *Oil Gas J.*, 4.7.40, 39 (8), 40.—The reasons why oil-wells should be drilled as nearly vertical as possible are detailed, and a discussion is given, showing why, if certain conditions exist, directional drilling is attempted purposely to deviate the hole from the vertical. Both cases, however, are similar, in that they require frequent and accurate surveys of the bore-hole.

Instruments used in surveying wells are described, those of the photographic recording types in some detail. The interpretation of survey records is then given. To know the location of any point of the course of a hole it is necessary to know

its true vertical depth, its latitude, and the extent of its departure from a datum point. The method of calculating these quantities is briefly given.

Directional drilling using whipstocks is next discussed, and magnetic orientation of deflecting tools is detailed.

Finally, the paper describes polar core orientation. By this method the direction of the dip of the core sample is obtained from the magnetic properties the sample acquired from the earth magnetic field. The instrument which is described for determining the orientation operates automatically, is self-checking, and operates electrically. It is assembled on a large oak table with the magnetic system on one end and the recording system on the other. The core is held in a core-holder, and rotates in a horizontal position below an astatic magnetic system one full revolution in about 30 min. Photographic records are taken by means of a mirror and spotlight for two revolutions, the second being in reverse direction of the first. The instrument, records, and the method used in interpreting the charts are illustrated.

A. H. N.

**1256.\* New Portable Rig Uses Torque Converter and 90-ft. Folding Mast.** T. P. Sanders. *Oil Gas J.*, 11.7.40, 39 (9), 53.—A tyre-mounted drilling rig is described, designed for 6000-ft. drilling, and using a hydraulic torque converter to combine steam-engine power characteristics with the portability and fuel economy of the internal-combustion engine.

Although the rig is mounted on a base small enough to travel on the highways, it incorporates a 90-ft. derrick, which is raised and lowered completely intact by means of hydraulic cylinders. The derrick has a capacity of 200 tons, and the upper 60 ft. of it can be removed and carried individually if required.

Other unusual features include hydraulic breakout lines and a rotary head which grips the kelly over a 48-in. length to minimize whipping of the drill stem. A. H. N.

**1257.\* Oil-field Development and Drilling Methods.** K. C. Slater. *Petrol. Engr.*, Midyear, 1940, 11 (10), 13-16.—In this review of methods and principles employed in oil-field development the importance of well-spacing programmes is emphasized, but it is pointed out that well spacing is still largely decided by arbitrary assumptions based on past experience. References are given to literature dealing with this as well as problems of appraising reservoir conditions, proration, etc.

Deep-drilling activities are reviewed. Efforts are being made to obtain greater economies in drilling, and these have resulted in studies of rate-of-penetration. It was revealed that one-third of drilling time was spent on running in and out of the hole, which fact emphasized the importance of bit service. Improvements in bits has resulted in a reduction of the running in and pulling out time to one-fifth the total drilling time. Drilling speed has increased from 5 ft. to 50 ft./hr. and bit footage from 75 ft. to 1000 ft.

The Carter core-barrel is briefly described and pressure coring is reviewed generally. This process is still being perfected. Electrical coring has been improved by the addition of several new devices, particularly those dealing with testing the mud stream continuously for oil and gas and salt water. A somewhat recent system is logging a well whilst drilling by utilizing the drilling-string and bit as electrode.

An innovation in well-cementing is mixing radioactive materials in the cement, which process makes it possible to estimate the position of the cement behind the casing. Methods of reducing channelling include mixing bentonite with the cement and using certain mechanical centralizing means for the casing.

In well-completion practices, gravel packing is now advocated as a proper method of completing wells in unconsolidated sands. Multiple-sand completion practices are reviewed, together with the use of drillable liners for such purposes. A. H. N.

**1258.\* Advancement in Drilling Technique in California.** W. A. Sawdon. *Petrol. Engr.*, Midyear, 1940, 11 (10), 108.—There was no new depth record in California last year, but 10,000 ft. deep wells have become more common than was previously the case. Speed in drilling has increased, and the record is believed to have been broken.

Rotating speeds as high as 750 r.p.m. have been tried, but only one company used speeds exceeding 500 r.p.m. Remarkably fast, straight holes have been drilled with

high rotating speeds, but intelligent co-ordination of equipment and technique was found essential.

In surface equipment, two new draw-works of a size larger than any previously used have been put in service during the last six months. Those are described. The contemplated use of  $1\frac{1}{2}$ -in. lines has not materialized, and it appears that  $1\frac{1}{4}$ -in. will still be the most generally used in deep fields. Latest types of blocks are constructed with drums instead of shafts, which fact makes the sheaves virtually rims with large-diameter roller bearings. Descriptions of other items are given for surface equipment, including derricks, rotaries, boilers, etc.

As high pressures and large volumes of circulating fluid have become necessary in deep-drilling operations, there has been a tendency to use as large a diameter drill pipe as is practicable. A  $5\frac{9}{16}$ -in. drill pipe is frequently employed to depths ranging from 8000 to 10,000 ft. The use of long drill collars to give weight just above the bit, and thus keep all the drill pipe in tension, has been an important factor in keeping holes straight.

Mud fluids used have not been excessively heavy. Probably the greatest weight being carried is 100 lb./cu. ft.; however, the average is only 78-85 lb./cu. ft., and weights above 90 lb. are uncommon. Weighting material is employed. Chemical treatment is most widely applied for deflocculation and reduction of viscosity. Two of the complex phosphates are used, tetrasodium pyrophosphate and sodium tetraphosphate.

Two new dogassors have been put into service, and these are described. A. H. N.

**1259.\* Drilling Time Studies.** H. L. Flood. *Petrol. Engr.*, July 1940, **11** (11), 23-24.—Drilling-time studies involve no complications either in apparatus or drilling practice. They impose on the driller the routine job of recording the time required to drill a given number of feet of hole. The usual procedure is to note the time required to drill 2 ft., 5 ft., or 10 ft. of hole. Readings taken at these intervals generally result in a drilling log of sufficient accuracy to disclose information concerning the formations drilled, and serve as a reliable check on cores taken periodically or on the results of electrical logs.

Charts are reproduced correlating drilling-time curves with electric logs for a well, and variations in drilling time are supported by evidence from the electric log to show that a pay sand has been penetrated. A. H. N.

**1260.\* Use of Bulk Cement in Wells.** Anon. *Petrol. Engr.*, July 1940, **11** (11), 74.—The use of large-capacity cement hoppers is advocated as reducing time required to mix and place slurry in deep wells. A. H. N.

**1261.\* Drilling Footage near Peak as Wells go Deeper.** Anon. *Oil Wkly.*, 15.7.40, **98** (6), 19-20.—Statistical data are presented for drilling activity and depths reached this year. Average drilling depths show an increase as compared with last year. The total footage is increased by greater average depths and also by an increase in the number of wells drilled. A. H. N.

**1262.\* Depth Measurement by Means of Multiple-Strand Wire Lines.** H. E. Gross and J. P. Hays. *Oil Wkly.*, 22.7.40, **98** (7), 13-17. *Paper presented before American Petroleum Institute.*—The tolerance between the various methods of depth measurement should be 1 ft. in the first 4000 ft., and should not increase more than 1 ft./additional mile depth. Greater discrepancies show poor workmanship.

The cable is always under full tension of its own weight, as it is lowered, and therefore no correction for stretch need be applied when stringing in. As a pipe is usually measured as it stands on the rack, this fact does not apply to the case of depth measurement with a pipe. Elongation correction due to temperature is customarily ignored in depth measurement.

Standard rigs, cable-tool drilling machines, and spudders employ two multiple-strand wire lines for drilling a well. In depth measurements it is both time-consuming and impracticable to measure the entire length of the wire line. The appropriate procedure is to measure very carefully the distance over the derrick between "fixed points" at

the wire-line spool and at the well-head. This distance is the "yardstick" for subsequent measurements. The measurement over the derrick is best obtained in calm weather, preferably about sunrise.

The authors describe in detail and illustrate by diagrams the details of taping over and of measuring with sand-line, drilling-line, spudder, and with portable drilling machines. Accuracy is stressed in all operations.

In cases of rotary drilling units the coring line is used in a similar manner to the sand line. Finally the special methods peculiar to electrical logging, gun-perforating, and well-shooting operations respectively are discussed. In these cases errors inherent in counting mechanisms resulting from inertia slippage and incorrect diameter of the sheaves and lines require adjustments to the positive and precise measurements that should be obtained with the drill pipe or cable.

A. H. N.

**1263.\* Factors Influencing the Bond between Oil-well Cement and the Formation.** P. H. Jones and D. Berdine. *Petrol. World*, June 1940, **37** (6), 26. *Paper presented before American Petroleum Institute.*—Cement channelling and factors influencing the bond between set cement and formation were investigated in a series of forty-two tests using relatively large-scale apparatus simulating conditions prevailing during the cementing of oil-wells. The extensive paper is well illustrated photographically.

It is concluded that channelling and chimney formation of cement in the annulus are unlikely in the immediate region of the shoe, but may occur near the top of the cement column.

Wherever cement slurry is applied opposite formations having appreciable permeability, a residual mud cake will remain between the set cement and the formations unless specific means are employed to effect its removal. The presence of collars, movement of casing, or circulation of water may slightly reduce the thickness of the mud cake, but will not remove it completely.

Where casing rests against the walls of the hole, residual cakes will be thicker than normal. There is a tendency for the cement slurry to be excluded from such regions of proximity, thus leaving longitudinal stringers of mud cake with no cement between the casing and the formations.

Three methods were found effective in removing mud cakes: (1) Hydraulic action by direct impingement of fluid jets (such as that induced by down-whirlor shoes) against the walls of the hole. (2) Mechanical scraping by using suitable mechanical devices on the casing. This is effective only over areas where scrapers or scratchers make a bearing on the wall of the hole. (3) Acid treatment gave best results under atmospheric pressure conditions. Laboratory tests at high pressure indicate but do not prove that effective mud-cake removal under these conditions may be obtained.

A. H. N.

**1264.\* Rotary Drilling Mud Testing and Control.** J. A. McDonough and C. F. Bonnet. *Petrol. World*, July 1940, **37** (7), 36.—The paper describes the important properties of mud; methods for testing are given, and practices are outlined for maintaining muds in condition for fast and safe rotary drilling. The properties studied are weight of mud, water loss and cake thickness, sand content of mud, gel strength, pH value, and salt content, and finally viscosity and chemical treatment of muds. In each case a very brief outline of the significance of each property is given, followed by typical characteristics of a well-conditioned mud and a brief description of the methods or apparatus used in assessing the characteristic quantitatively.

The paper is descriptive and generalized in treatment.

A. H. N.

**1265.\* Technical Trends.** Anon. *Petrol. World*, July 1940, **37** (7), 48.—The effects of water from the drilling mud on the formation drilled are discussed and an oil-base drilling fluid is described. This fluid is made up of 55% 38° stove oil, 30% ground calcium carbonate (95% through 200 mesh), 5% lamp-black, and 10% air-blown asphalt. The reason for incorporating lamp-black is to keep the calcium carbonate in suspension for weighting the fluid and for using asphalt is to build a thin cake on the walls. Those wells drilled with oil-base fluids in the hole showed a better productivity index than those drilled with normal clay fluids.

A new pipe-thread lubricant is described. It consists of 50% aluminium soap grease and 50% graphite. The characteristics and specifications of the lubricant are given.

A new cementing procedure adopted recently showed good results. The slurry consisted of 50% cement and 50% calcium carbonate. After setting the cement the casing was perforated in five different zones with inhibited acid stratified against the perforation zones. The acid followed the bullets into the cement, thus dissolving the shattered particles and enlarging the drainage areas. This cementing procedure was used in the completion programme of a well.  
A. H. N.

**1266.\* Effects of Acid on Mud Cakes.** Anon. *Petrol. World*, July 1940, 37 (7), 51.—In tests performed to show the effect of hydrochloric acid on mud under high pressures a small piece of mud was separated from the acid by a cellophane diaphragm, both mud and acid being in a pressure chamber fitted with a glass window and the necessary instruments to maintain and measure the pressure and temperature obtaining in the cell. The diaphragm was ruptured and the effects of the acid were visually observed and recorded photographically. Five types of mud were tested.

The conclusions reached are: (1) Acidizing mud cakes breaks down the colloidal character of the cakes and gives them a granular structure. (2) The addition of an acid soluble constituent—*i.e.*, calcium carbonate—to the mud hastens the flocculation of the cake with acid, probably because the acid penetrates more easily as the soluble constituent is removed. (3) Calcium carbonate will dissolve in 15% hydrochloric acid under 1000 lb./sq. in. pressure. The carbon dioxide evolved in the reaction is completely dissolved in the water present.  
A. H. N.

**1267.\* Conditioning Drilling Mud.** F. C. Bowman. *Petroleum World*, July 1940, 37 (7), 53-54.—Six requirements are considered of fundamental importance in drilling muds, and the effects of adding sodium pyrophosphate to the mud on the properties of mud connected with these requirements are studied. These requirements are, in brief: (1) The fluid must lubricate the drill bit. (2) It must hold the cuttings in suspension until it reaches the surface. (3) It must allow the cuttings to settle outside. (4) It must be heavy enough to prevent blow-outs of gas under pressure. (5) It must provide a seal for the formations. (6) Its viscosity should be sufficiently low to make easy pumping and settling out.

The addition of pyrophosphate of sodium helps in all these requirements, except item (4), where the weight of the fluid is not affected to any appreciable extent. The quantity of sodium pyrophosphate used is popularly set at 1 lb./ft. drilled. In a 10,000-ft. well large quantities are evidently used.  
A. H. N.

**1268.\* Looking to the 20,000-ft. Well.** E. K. Parks. *World Petrol.*, July 1940, 11 (7), 46-53.—The paper constitutes an inquiry into the physical and economical limits of depths to be reached in oil-well drilling. In studying the obstacles to reaching a 20,000-ft. depth, the drilling experience obtained in drilling to 15,000 ft. is analysed. The limitations appear to be: (1) The hole must be straight. (2) The mud must be constantly controlled in physical character. (3) The wire rope used in hoisting drill pipe from 15,000 ft. is excessively loaded. (4) The 3½-in. drill pipe at 15,000 ft. is loaded to the limit of its tensile strength under normal conditions, allowing no margin for extra pull in case of emergencies. (5) Casing for the well sets limitations in the clearances necessary between casing and other items in the well. Each item is discussed separately.

In the engineering section the high temperatures encountered with depths will create difficult problems. The effects of high temperatures and pressures will be particularly severe in mud conditioning, in considerations of corrosion of metals, and in cementing.

In production practice, as soon as natural flow ceases, the process becomes expensive, especially if complicated by emulsions, sand, water, wax, etc.

A study is made of well spacing, cost of drilling, and economics of such a project. Finally, it is concluded that: (1) A well 20,000 ft. deep appears not only as a possibility but as an approaching reality. (2) The chances for profit under present conditions are so narrowed that the 20,000-ft. well may be expected only as a result of some extended prospect. (3) There is no technological reason why such a well should not produce oil and gas at a commercial rate. (4) Development of a 20,000-ft. oil reservoir will require great geological skill and constant expert engineering supervision, in order

to reduce the elements of chance. (5) The high yields required for a pay-out will greatly restrict the number of wells to be drilled into a unit reservoir. (6) The high yields required will tend towards an extension of the pay-out period. (7) The great cost will require minimum royalties and a reasonable assessed valuation on the discovery holdings in order to avoid confiscatory taxes. (8) The cost will discourage competition and encourage unit operation of the deep-well field. A. H. N.

**1269.\* Drilling Conditions in Turner Valley.** V. Taylor. *World Petrol.*, July 1940, 11 (7), 68-71.—Averaging but 41 ft./day and sometimes getting as little as 2 ft. per bit, nevertheless an active drilling campaign continues in Canada's Turner Valley even in excessively cold weather. Some 96% of Canada's domestic production of oil comes from this field.

Drilling equipment and practice are described. Steam is used on all rigs, as there is an abundant supply of water and gas. Rock bits are used exclusively.

Certain preparations are made for winter drilling operations. The derrick is covered in as much as possible and steam heaters are used extensively in order to prevent freezing of various parts of the equipment. It is essential to blow out all mud-lines and water-lines with steam when not in use, and it is also necessary to hook up rat hole so that circulation can be maintained through the kelly when it is not in use. Considerable expense is thus entailed in rigging up for cold-weather drilling. A. H. N.

**1270.\* Deeper Drilling Requires Improved Instrumentation.** G. L. Kothny. *World Petrol.*, July 1940, 11 (7), 76-81.—In temperature measurements of deep holes, charts show that the "out-run" survey curve is always higher than the "in-run" curve. This is probably due to the time lag, as the instrument will record the temperature of the air immediately surrounding it within the protective casing, and the temperature of this air is materially lower than that of the well fluid or casing. The maximum temperature recorded in two charts was on the out-run, and at a point 2000 ft. above the bottom of the well in both cases.

Surveys made with multi-shot instruments in which a magnetic compass is used for recording the direction may be subject to erroneous recording, due to magnetic fields and influences from sources other than the earth. A chart is worked out giving the correction to be applied to recordings because of the inclination of drill pipe, tubing, or sinker bars of various lengths and inclinations and possessed of a magnetic pole strength of 300 E.M.U. Further, a table is given for errors due to the inclination of the instrument relative to the axis of the drill pipe or casing. Rubber star-shaped guides help to minimize this source of error.

In directional drilling it is necessary to find the orientation of the deflecting tool. A new and successful magnetic method of orientation is described and a sectional drawing of the instrument is given. This is claimed to have the advantages of speed, cheapness, accuracy and self-checking, and of saving rig time.

Finally, core orientation is fully discussed, the instruments used are illustrated, and a specimen report is presented. Cores which have been stored for several years in the core sample-room, as well as cores shipped from foreign lands more than 10,000 miles distant, have been successfully oriented by this method. The process uses the magnetic-core orientation method. A. H. N.

**1271.\* Hydraulic Couplings in Field Applications.** M. T. Archer. *World Petrol.*, July 1940, 11 (7), 81-85.—The simplest form of hydraulic coupling is the traction type. The nature of the rotary drilling, however, imposes the necessity for speed control over a considerable range both at the table and at the slush-pumps. Such control can best be secured by using the variable-speed couplings, preferably the recently introduced scoop-control type.

In connection with mud pumps, a safety factor is provided by using the coupling. Since the pump stalls, the engine need not stall too, as the coupling will slip 100% without overloading the engine. The coupling will naturally dissipate by convection approximately 7-10% slip without overheating the oil. Allowance for higher slip is made by water cooling.

When hoisting, the instantaneous load is severe and the slip of the coupling may be temporarily great, but the short hoisting cycle is followed immediately by an idling



cycle which permits cooling sufficiently to offset the overloading. Nevertheless, it is deemed advisable to provide cooling by auxiliary means, as the rotary table is connected to the hoisting engine in the majority of cases.

Layout of various typical installations and experience gained in different fields are described. A. H. N.

**1272.\* Fluid Coupling Applied to Rotary Drilling Equipment.** G. V. Davies. *World Petrol.*, July 1940, 11 (7), 86-89.—The introduction of fluid coupling, the Vulcan-Sinclair type at first, into rotary drilling equipment has overcome most of the difficulties inherent in the use of internal-combustion engines. This fact is due to the following essential characteristics: a practically complete connection and disconnection of the drive with a continuously running engine; a perfect cushioning medium, since power is transmitted by virtue of the kinetic energy of the oil circulating in the coupling, thus damping out torsional vibrations from the engine and absorbing shock loads from the driven machinery; a completely smooth take-up simply by accelerating the engine and allowing the load to be picked gradually while running; an ability to transmit power equally well in either direction, thus overcoming the difficulty of reversing; an absence of moving parts subject to wear and consequent replacement, with a remarkable simplicity and low initial cost; and a positive safeguard against stalling of the prime mover by overload while transmitting the overload to the driven shaft.

The working of the coupling is briefly explained and well illustrated. The fluid with which the coupling is filled is driven outwards by the centrifugal force transmitted by an impeller with radial vanes, and as the runner always rotates at a slower speed than the impeller, the difference in centrifugal force causes the fluid to circulate around an annular core, and thus act as an energy transmission medium.

The scoop-tube type of coupling is further explained and its advantages are studied. Infinitely variable speed regulation can be obtained over a range of five to one. The speed of a rotary table was reduced from 100 r.p.m. to 6 r.p.m. by reducing the engine speed from 600 r.p.m. to 200 r.p.m. and operating the control. The same results can be obtained in the reverse direction by the use of a double-ended scoop and a reversing engine.

An impulse or momentum start can be applied by closing the scoop-tube control, running the engine up to speed, and then opening the control, and thus a substantial overload torque may be applied for freeing an obstacle. A. H. N.

**1273. Arrangements of Filter Tubes in Petroleum Wells.** F. R. Ruiz. *Bol. Inform. Petroleras*, March 1940, XVII (187), 72-78.—This article refers in the first instance to the conditions at Comodoro Rivadavia, where the strata consists partly of sands and partly of more friable material. The commonest form of filter tube is a tube with circular perforations. It is pointed out, however, that this type was found to be ineffective. Two types of filter, the MacEvoy and the Kobe, are described, the latter being the type finally adopted. This type of filter is made up by plugging the circular perforations with plugs provided with grooves of a particular shape and section. In order to arrive at a satisfactory design one is dependent on a granulometric analysis which sufficiently nearly anticipates the character of the solids at the bottom of the well. Interesting curves are given in which the percentage retained is plotted against the size of the grains and the size of the opening in the grooves. These curves are taken from the Manantiales Behr. Similar curves are shown for Calota Cordova in which the conditions are more favourable owing to the fact that the horizon consists of a simple layer of sand. The effect of water is also dealt with very fully.

H. I. L.

**1274. Drilling Patents.** J. B. Graham and R. G. Mayer. U.S.P. 2,206,184 and 2,206,185, 2.7.40. Appl. 21.3.39 and 10.6.39, respectively. Apparatus for guiding and stabbing successive sections of pipe such as oil- and gas-well casings.

T. A. Creighton and T. E. McMahan. U.S.P. 2,206,222, 2.7.40. Appl. 24.7.39. Well-drilling tool, being a bit of special type.

G. E. Cannon. U.S.P. 2,206,389, 2.7.40. Appl. 27.9.39. Method of cementing

wells consisting of allowing fast-setting cement to form a plug at the gas-oil interface, and subsequently cementing with slow-setting cement below the plug.

J. H. Sheplor. U.S.P. 2,206,677, 2.7.40. Appl. 8.4.39. Method and means for preparing wells for cementing by pumping a suspension of abrasive material in water to remove mud sheath.

A. Boynton. U.S.P. 2,206,873, 9.7.40. Appl. 28.10.38. Leakless right and left tool joint.

A. L. Smith. U.S.P. 2,206,922, 9.7.40. Appl. 8.8.38. Means and method of detecting the presence of oil in drilling mud by subjecting mud to ultra-violet light and observing the fluorescence caused by oil.

R. D. Haas. U.S.P. 2,207,005, 9.7.40. Appl. 18.10.38. Pipe and tool joint.

L. W. Stahl and R. L. Foster. U.S.P. 2,207,112, 9.7.40. Appl. 25.2.38. Liner construction for slush pumps.

F. W. Hild. U.S.P. 2,207,149, 9.7.40. Appl. 8.10.34. Blow-out preventer.

J. A. Zublin. U.S.P. 2,207,187, 9.7.40. Appl. 15.7.38. Combined fluid and rotary driven drilling bit the cutters of which are rotated by discharge of fluid against them.

J. A. Zublin. U.S.P. 2,207,188, 9.7.40. Appl. 23.1.39. Drill bit.

F. W. Hild. U.S.P. 2,207,199, 9.7.40. Appl. 26.4.37. Blow-out preventer having a hollow packer.

C. A. Lundeen. U.S.P. 2,207,203, 9.7.40. Appl. 14.5.38. Support for upset pipe or rod utilizing slips on an inclined plane.

O. Hammer. U.S.P. 2,207,345, 9.7.40. Appl. 23.3.38. Method and means of cementing wells using a guide-tube at the bottom of the casing.

A. F. Sorben. U.S.P. 2,207,418, 9.7.40. Appl. 5.4.39. Bottom dumping cement bailer.

R. T. Royo. U.S.P. 2,207,469, 9.7.40. Appl. 4.1.39. Casing hanger.

E. Russel. U.S.P. 2,207,478, 9.7.40. Appl. 30.12.36. Apparatus for spraying and casing well with a quick-setting cement or the like.

C. St. J. Bromner and C. M. Potter. U.S.P. 2,207,505, 9.7.40. Appl. 5.4.35. Drill-pipe orienting tool.

J. H. Williams and S. Ackal. U.S.P. 2,207,649, 9.7.40. Appl. 8.9.39. Oil-well fishing-tool.

L. L. Thompson. U.S.P. 2,207,766, 16.7.40. Appl. 7.3.38. Rotary drill bit.

J. D. Hughes. U.S.P. 2,207,920, 16.7.40. Appl. 28.10.37. Expanding foot-piece for whipstocks.

E. E. Anderson. U.S.P. 2,208,011, 16.7.40. Appl. 14.4.39. Inside tubing cutter.

J. D. Eisler. U.S.P. 2,208,147, 16.7.40. Appl. 26.8.38. Photo-electric inclinometer for testing the deviation of a bore hole.

N. Miles. U.S.P. 2,208,194, 16.7.40. Appl. 12.8.39. Safety cage for oil derricks.

J. H. Schreiber. U.S.P. 2,208,197, 16.7.40. Appl. 16.6.37. Joint breaker and cathed.

G. R. Potho. U.S.P. 2,208,388, 16.7.40. Appl. 11.12.39. Oil-tool spinner for an oil rig rotary table.

L. L. Thompson. U.S.P. 2,208,530, 16.7.40. Appl. 3.2.38. Rotary well drill bit.

D. Scaramucci. U.S.P. 2,208,603 and 2,208,601, 23.7.40. Appl. 17.8.39. Apparatus for cementing wells consisting of a measuring device for determining the position of an object like the top plug in a well. It is a sounding-line, a weight attached to the line and an object adapted to be positioned within the well and arranged to be magnetically engaged with the weight. The second patent incorporates an electromagnet.

H. C. Lawton. U.S.P. 2,208,766, 23.7.40. Appl. 16.1.39. Method of sealing off formations by the controlled formation of a silicic acid gel within the pores, using aqueous solution of a silicate, and a non-metallic salt of a weak base in basic solution.

A. H. N.

## Production.

**1275.\* Progress of Gravel-Packing in California.** Anon. *Petrol. World*, June 1940, 37 (6), 47.—The paper deals with the history, theory and methods, and the present status and outlook for gravel-packing in California.

Gravel-packing is primarily intended to stop sand production, thus almost entirely eliminating those features which raise production costs. Two photographs show examples of correct and incorrect choice of gravel size, in the former the sand migrating only imperceptibly into the gravel pack, whereas in the latter the entire pack is filled with sand, resulting in drastically reduced flow capacity. Other advantages of gravel-packing include providing a larger open hole with better drainage conditions, the action of the pack as a gas anchor, and the possibility of deeper pump setting and lower fluid level being presented by gravel-packing.

The most commonly used method involves wall-scraping to about 15 in. in diameter, and then circulating the gravel down through the casing and outside the liner through ports in the hanger, using thin mud. A description is also given of the chief types of pre-packed liners available in California.

A. H. N.

**1276.\* Huge Additional Reserves Wait on Improved Production Methods.** L. C. Uren. *World Petrol.*, July 1940, 11 (7), 54-57.—The charges of excessive waste of oil both in production practices and above-ground storage usually levelled against producers are shown to be without much basis in many instances. Recent improvements in methods of exploitation of oil-fields are reviewed and the spirit of conservation in production practices is made manifest.

On the other hand, great quantities of oil are still left in the reservoirs because no recovery methods yet discovered are sufficiently economical, with present-day oil prices, to produce more than a part of the oil actually present in the reservoir. It is estimated that between 67,500 million and 110,000 million brls. of oil must have been left in the ground in present known fields. The actual reserve estimated as being recoverable by present methods of production is only 18,000 million brls.

It appears that the main consideration in these problems is an economical one intimately connected with the price of recovered crude and cost of production.

A. H. N.

**1277.\* High Water-cut Samples easily Taken.** Anon. *Oil Wkly*, 8.7.40, 98 (5), 22.—Faced with the problem of taking accurate samples on a lease on which a number of wells were going to water quite rapidly, one superintendent of a large oil company devised a system of obtaining regular water-cut samples without incurring the expense of adding costly equipment or enlarging the existing tank facilities. The system is described, and consists essentially of weigh-meter which is fitted at each tank setting on the lease, and which records the gross fluid as it comes from the well, and of a constant-level arrangement for the water after separation in the tank. A. H. N.

**1278.\* Elevated Pumping Unit in Over-flow Area.** Anon. *Oil Wkly*, 15.7.40, 98 (6), 36.—A pumping unit elevated on a platform in order to continue functioning during periods of overflow in the lease, and which is fitted with a special heater, as the oil is highly paraffinic, is described.

A. H. N.

1279.\* **Raised Structure Guards High-pressure Well.** Anon. *Oil Wkly*, 22.7.40, 98 (7), 12.—A well-head structure is described, which appears to have been designed with a view to ruggedness, safety for workers, and protection from damage by cattle, floods, and tornadoes. The tree is a 10,000-lb.-test type, and the high-pressure wells are 10,300 ft. deep.

A feature of the system is a flow-valve in the tubing string which closes automatically against high rates of flow—a valuable asset if surface connections are broken by flood or a tornado. Another feature is a low-pressure manifold connected to the tree by pipe-bends which are effective in abating turbulence. A. H. N.

1280.\* **Industry Faces Economic Crossroads.** W. L. Baker. *Oil Wkly*, 29.7.40, 98 (8), 41–45.—It appears that revenues are diminishing from producing wells, and that unless the problem is solved logically it may assume serious proportions. Five possible solutions are discussed. The first three are: (1) to raise the price of crude; (2) to increase consumption; (3) to improve methods of development at cheaper costs. All three suggestions suffer from the fact that they are beyond the immediate control of the operator and, further, if they were successful they would induce additional drilling activities, and thus, after a temporary relief, the problem would have to be faced again in a probably more acute condition.

Wider well spacing and unit control of pools are offered as the only logical ways of treating the problem. Advantages of wider spacing are listed as, briefly, (1) wider spacing will readjust the equilibrium of supply and demand; (2) capital expenditure per acre developed is less with wide spacing; (3) fixed charges are less; (4) daily allowable per well will be greater as wells decline; (5) operating costs, gross and per barrel, are less; (6) dissipation of reservoir energy is reduced; (7) volume of salt water handled is less; (8) part of funds now used in intensive drilling becomes available for wildcatting and discovery of new fields.

Unit operation is advocated because there is maximum economy of operation; fewer wells are needed; reservoir control is made practicable; individual risk is minimized; a stabilizing effect is imposed on the market; it increases per-acre yield of oil; an increased value is created for gas; it permits adjustment of production rate to the producers' needs; it effects savings on pipe-lines, storage tanks, and plant capacity; it makes possible the practices of pressure maintenance, repressuring, water flooding, and recycling. A host of other reasons are advanced. A. H. N.

1281.\* **Prorated Production A Minimum Profit Level.** Anon. *Oil Wkly*, 29.7.40, 98 (8), 46–52.—The steadily diminishing revenues from producing wells in recent years have already reached the minimum economic level at which numerous wells may be operated, and it is claimed that if the trend continues its downward tendencies oil-producers will be faced with an extremely serious financial situation in the very near future. It was felt that despite the probable lack of absolute accuracy there was a need for an estimated measure of the relationship between costs and income. Consequently, by use of data known and generally accepted by the industry and a system of weighted averages and "present worth appraisals," an attempt was made to compare the average prospects for profits from new drilling development that were in existence in the eight prorated states during each of the years from 1935 to 1939. No absolute accuracy was claimed for the results, but they were believed to possess a certain validity.

An acute condition of diminishing income return per dollar invested is shown. This paper does not suggest the remedy, but only the situation is discussed. The remedy is discussed in a preceding paper. [Cf. abstract no. 1280.] A. H. N.

1282.\* **Increased Efficiency through Use of Smaller Pumps.** T. P. Sanders. *Oil Gas J.*, 4.7.40, 39 (8), 45.—In wells pumped on the beam more production is lost due to installing pumps that are too large than because of using pumps that are too small. Two general classes of wells commonly suffer from too large pistons:

(1) Deep wells, where the string of sucker rods is more than 4000 ft. long. In such a well large plungers cause excessive rod stretch, resulting in losses due to loss of stroke length in excess of the gain of using the large plunger.

(2) Any well in which a pump-off condition occurs. In such a well a relatively small pump reduces the polished-rod load, and slippage past the plunger is minimized. Also if pounding of the fluid does occur, the small plunger minimizes the effects of the shock on the equipment.

A table gives maximum recommended plunger sizes for wells of various depths, from 4000 ft. (maximum plunger diameter, 2½-in.) to 8000 ft. (maximum diameter, 1½-in.).

A. H. N.

**1283.\* Operating Efficiency Increased by Standardization.** N. Williams. *Oil Gas J.*, 11.7.40, 39 (9), 57.—Standardization of all lease production equipment is being carried out by a Texas company. This not only applies to completely new installations, but also as old lease facilities, such as stock-tank batteries and separator hook-ups, well connections and assemblies, and other units need attention or replacements they are made to conform to the uniform types and designs adopted as the field is developed. The paper details various items so standardized both in surface and subsurface pumping equipment.

It is claimed that this work is contributing markedly towards efficiency of working the field, towards reducing greatly the number of items necessary to be carried in warehouse stocks and towards simplifying and facilitating installation and maintenance of the various operating units.

A. H. N.

**1284.\* Subsurface Pump Performance.** S. B. Sargent. *Oil Gas J.*, 11.7.40, 39 (9), 58.—*Paper Presented before American Petroleum Institute.* The first part of this short paper deals with theoretical and actual sequence of events which occur in a subsurface pump in action. Typical dynagraph data are presented for various stages of plunger movement in the barrel, and these are explained and interpreted in the latter part. Cards are also shown when the pump is handling gas with the oil.

It is concluded that there are a great number of factors influencing pump operation that cannot be readily determined without the use of instruments to measure their relative magnitudes. Each factor taken by itself is quite simple and is easily explained by fundamental laws of either hydraulics or mechanics.

A. H. N.

**1285.\* Chart for Computing Volume.** Anon. *Oil Gas J.*, 11.7.40, 39 (9), 65.—A chart is presented for computing the volume of gas being injected into input wells, or of gas obtained at casinghead in calculating gas-oil ratios and using an orifice meter. Given orifice size in inches, specific gravity of gas (compared to air), gauge, and differential pressures in lb./sq. in. and inches of water, respectively, the volumetric rate of flow of gas in cu. ft./day is found to an accuracy of 5%, using the chart to the scale which is presented. On a considerably larger scale it is believed that the chart could be read to a maximum error of 2%, or practically to the error of the usual orifice meter employed.

An example illustrates the use of the chart.

A. H. N.

**1286.\* Low Producing Rates Waste Reservoir Pressure.** T. P. Sanders. *Oil Gas J.*, 11.7.40, 39 (9), 66.—Actual field evidence indicates that a low rate of flow can be, and usually is, even more wasteful of reservoir pressure than is wide-open flow. While open flow is not recommended, it is preferable to too severe restriction, which tends to bleed off an abnormally high proportion of gas, leaving "dead" oil in the reservoir.

Wells with small allowables that are made to flow at low rates for 24 hr./day almost invariably suffer from extreme separation of oil and gas in the tubing. Correction of this condition can be brought about simply by adopting faster flow, with minimum gas-oil ratio, and shutting the wells in for the remainder of the day after the allowables have been made. For determining the best rate of flow for a well there is no substitute for gas-oil ratio.

For wells which use a 2-in. tubing, material assembled shows that wasteful conditions usually occur when the rate of flow is restricted below 10 brls./hr.

A. H. N.

**1287.\* Economic Aspect of Water Flooding.** L. C. Converse. *Oil Gas J.*, 18.7.40, 39 (10), 18-19.—This paper is devoted to economic studies in the Mid-Continent

fields. The crude is produced at low cost as compared with deeper and newer fields, and this fact is due, in the main, to three causes: (a) discovery and leasehold cost; (b) development cost; and (c) lifting cost, all of which costs are low. After a conservative estimate, leasehold costs are given at 6 cents/brl.

The development costs are again low, due for instance to the fact that for a water-flooding project most of the wells required are already drilled. The lifting costs are affected by the size of the shot hole, the effective permeability of the sand, the viscosity of the oil, the pressure applied, and the resistance or distance between input and output wells. These factors are studied specifically in Bartlesville sand.

In estimating the total cost of a barrel of crude recovered by water flooding these old sands, 6 cents are allotted to leasehold cost, 10 cents to development, 10 cents to lifting, 7 cents to engineering and supervision, and 10 cents to overhead charges. Thus total cost of the crude is 43 cents/brl. A. H. N.

**1288.\* Electrifying Oil Properties and Service Restoration Systems.** O. Dowzer. *Oil Gas J.*, 18.7.40, 39 (10), 41.—In the electrification of oil-field properties several factors must be considered in determining whether the power is to be purchased or privately generated. These factors, methods of installing secondary circuits, and means of restoring service are discussed.

During the past few years the central lease power plant or skid unit for the purpose of generating current to serve fifteen or twenty motor-driven pumping units has become quite popular. These units usually consist of small gas or diesel engine-driven generators equipped with automatic governors and switches generating at 440 volts. The motors run on 440 volts, whilst a transformer steps the voltage down to 110 volts for lighting. The system is economical, and two men per shift are sufficient to operate it.

It is pointed out that in service restoration generators are designed to take the full load of all motors working simultaneously, but not the starting loads of all motors simultaneously. This is due to the fact that a motor requires from three to five times its normal full-load running current for starting.

One method, requiring least investment, is to open the switches on all wells after a shutdown and to start them individually on service restoration. On the other hand, there is the most expensive of three methods suggested, that of fitting an under-voltage coil to each motor, and an automatic time switch. The motors will be automatically switched off on a breakdown, and on restarting any given number of motors may be started consecutively at, say, 10 or 15 sec. intervals.

The third method is intermediate in costs and time-consumption. Wells are fitted with under-voltage coils to shut them down on a breakdown in the generator, but are started by hand. The three methods are compared and contrasted. A. H. N.

**1289.\* Intermittent Injection Helpful in Repressuring.** T. P. Sanders. *Oil Gas J.*, 18.7.40, 39 (10), 54.—The basis for this short contribution is that experience in gas-drive work has shown that oil production will increase with increased gas input up to a certain limit. Beyond this an increase in gas may retard production. Further increase will cause excessively high producing gas-oil ratios, indicating channelling.

When intermittent injection is used, the permeable channels are invaded by oil from the adjacent tight sands during the shutdown periods. This oil is then moved to the producing wells when the gas is turned on. A. H. N.

**1290.\* Recent Trends in Petroleum Production Research.** L. C. Uren. *Petrol. Engr*, Midyear, 1940, 11 (10), 17-20.—Professor Uren deplors the short-sightedness of certain executives who spend hundreds of thousands of dollars in wildcatting and yet are reluctant to invest like amounts in research for better methods of recovery. Much of the advance in oil-field development and petroleum production methods achieved during recent years has been a direct result of research.

The paper reviews recent research projects on production and a list of 46 references is appended. Studies of reservoir fluids and reservoir mechanics are discussed, and these deal with phase behaviour of hydrocarbon mixtures, retrograde phenomena, mechanism of flow of gas, oil, and water through formations, and general principles of drainage. Formation sampling, sidewall sample takers, porosity, permeability,

and other core-analysis problems are next reviewed, together with researches on mud fluids, cementing problems, and gravel-packing. Finally, the materials used in well casing and drill-pipe manufacture are briefly studied.

A. H. N.

**1291.\* Recent Trends in Production Methods.** H. L. Flood. *Petrol. Engr*, Midyear, 1940, 11 (10), 35.—The trend of production methods appears to be towards the maximum utilization and conservation of reservoir energy. It appears also that light, inexpensive equipment that can be reclaimed and changed if its further use is not warranted is being used in increasing quantities.

Recording and interpreting adequate well data are being recognized as being of fundamental importance.

There has been a tremendous increase in the thought and attention accorded in the last year to methods of secondary recovery. Of greater significance than this is the fact that many fields are planned with a view to secondary recovery at some later stage of development, even at the very beginning of the exploitation and development programmes. Gas-repressuring and water-flooding are reviewed.

Pumping practices have seen improvements in load balancing, use of catenary pull rods and of electrically-powered units, better pumping engines, hydraulic pumping, gas anchors, and generally better technique. These are reviewed.

A. H. N.

**1292.\* Progress and Trends in Gas-lift Operations.** S. F. Shaw. *Petrol. Engr*, Midyear, 1940, 11 (10), 50.—Under present restricted production schedules, artificial gas-lift methods do not receive the attention they would command if the crude oil requirements were more nearly in line with the producible supplies.

Natural flow as a form of natural gas-lift process is briefly studied. A review is next given of artificial gas-lift as practised in Oklahoma City, Rodessa, various fields in Texas, Louisiana, Pennsylvania, and California, in Peru, and in other foreign fields under separate sections.

Restricted production resulted in the necessity of closing-in wells periodically, and hence the need for developing kick-off valves became great. A more scientific application of kick-off valves and "flow" valves than has been possible hitherto is gradually being worked out.

Studies into casing sizes and cost of gas and gas-lift are briefly reviewed and references are given.

A. H. N.

**1293.\* Developments in Production Practice in California.** W. A. Sawdon. *Petrol. Engr*, Midyear, 1940, 11 (10), 63.—At the present time there are approximately 18,850 wells in California capable of producing oil, 15,000 of which are actually producing. Nearly 90% of these are on the pump.

In several fields gas zones above the oil-producing formations have been utilized to produce the oil, controlled in a manner which has conserved the gas supply. This is being done with bottom chokes placed in the tubing string opposite a gas zone which has been separated from the lower oil formation by a packer.

There has been an increase in the use of hydraulic pumps, and in many cases multiple installation is used in which a number of wells receive power oil from a central location. In one certain field ten wells are produced thus.

A new method introduced recently in gas-lift districts is to put a plunger-lift shoe on the tubing when it is run for gas-lift; then when plunger-lift operation is necessary the plunger is dropped-in and the necessary surface connections are made.

A. H. N.

**1294.\* Progress and Trends in Water-flood Districts of Appalachian Area.** P. M. Phillippi. *Petrol. Engr*, Midyear, 1940, 11 (10), 76.—Perhaps one of the greatest strides forward in the art of water-flooding is the newly aroused interest in the shooting, and in particular the selective shooting, of wells. Eight major merits of selective shooting are enumerated, such as increased oil production per acre, decreased ultimate water consumption, quicker production and return of investment, etc.

There is a significant increase in the electrification of water-flooded areas, and this is probably due to the abnormally low price of this premier-grade oil, to proration, and to the cheap, easily available utility electric power.

The question of well spacing in a flooding area is chiefly an economic one, and ought to be solved on that basis, taking into account the properties of the particular sand under consideration.

Adoption of wide spacing means using high pressures. There is a critical pressure above which by-passing of the sand occurs to a serious extent. The maximum pressure to be used is just below the critical pressure, and it should not exceed 1 lb./ft. of depth.

A. H. N.

**1295.\* Electric Power for Oil-well Pumping.** J. E. Moody. *Petrol. Engr*, July 1940, 11 (11), 43.—Motors in use on modern pumping equipment may include one of the following: (1) single-rated, single-speed, normal-torque; (2) single-rated, single-speed, high-torque; (3) Star Delta, double-rated, single-speed; (4) double-rated, two-speed, constant-torque; and (5) double- or triple-rated, single-speed. The first two are the most generally used. The single-rated, single-speed, normal-torque motor is of the general purpose classification, but should an automatic time switch be installed, the second type is preferable, as it affords added safety factor on starting the well.

The performances of the various types are contrasted and compared with each other. Specimen calculations are given to determine the rating of a motor to be installed on a well. Recent installations indicate that 10-h.p. motors are generally ample to take care of present and future requirements.

A. H. N.

**1296.\* Motor-driven Submerged Power Pump.** W. A. Sawdon. *Petrol. Engr*, July 1940, 11 (11), 67.—A rodless pump for oil wells is described and its test performance figures and charts are reproduced. It is suitable for pumping 250 brls. or more of oil/day. Tests were performed at 3000 and 5000 ft. depths, respectively.

Briefly the pump and motor consist of an electric motor and a hydraulic transmission system to convert the high-speed rotary motion of the motor into a slow reciprocating motion, which is utilized in a conventional oil-well pump. The entire unit is enclosed in an outer jacket, the top of which is attached to the tubing production string and the bottom to the oil-well pump. Flow of oil after leaving the pump is upward through the annular space between the outer jacket and the case of the pumper mechanism. The passage of crude oil around the inner assembly keeps the motor and the power oil at approximately the same temperature as that of the crude itself.

A full description of the pump and its action is illustrated by a sectional drawing of the pump. The pump may be fitted with any ordinary auxiliary equipment such as gas-anchors and a blind cage for sandy wells.

A. H. N.

**1297.\* Deepening and Completing a Well in the Lisbon Field.** Pt. 6. P. D. Torrey and F. H. Miller. *Petrol. Engr*, July 1940, 11 (11), 70-72.—In this part of the paper production tests are detailed. The super-compressibility of the gas encountered is given in graphical form. The gravity and natural gasoline content of the separated gas are then studied and a summary of all the production tests performed on this particular well is given.

Bottom-hole pressure, physical analysis of the reservoir conditions, and recommendations for efficient rate of production conclude this part.

The paper will be concluded in a seventh part.

(Cf. abstracts Nos. 608, 754, 806, 994, and 1094 for previous parts.)

A. H. N.

**1298.\* The Behaviour of Oil and Gas under High Pressures and Temperatures.** Pt. 2. H. T. Kennedy. *Petrol. Engr*, July 1940, 11 (11), 77.—Experiments are described which have been performed under formation conditions and on a mixture of oil and gas as obtained from the reservoir. The apparatus consists of a glass pressure tube into which the oil is measured, and a measured volume of gas is introduced by mercury displacement. Pressure is applied, after mounting the glass tube in a metallic container, by a pump. Stirring is obtained by the reciprocating motion of an electro-magnet on a small steel ball inside the tube. Temperature is controlled by means of



an oil-bath. Volumes are measured by means of a cathotometer reading to 0.001 mm. Pressures are measured by a dead-weight gauge.

Charts giving the pressure-volume relationships are reproduced and analysed. It is shown that in a certain condensate reservoir, the original pressure of which has been 4200 lb./sq. in., 82% of the condensate will be in the reservoir when the last well is plugged in and abandoned, unless some pressure-maintenance system is adopted. Different systems are discussed. A. H. N.

**1299. Production Patents.** A. M. Herbsman. U.S.P. 2,206,187, 2.7.40. Appl. 19.6.37. Method of increasing production of oil wells consisting of introducing a solution of hydrochloric acid gas absorbed in a liquid which is immiscible with water, into the well.

J. M. Olson. U.S.P. 2,206,329, 2.7.40. Appl. 8.11.39. Tank gauge.

C. L. Murphy. U.S.P. 2,206,363, 2.7.40. Appl. 7.9.39. Valve for an oil tank.

D. W. Hoforer. U.S.P. 2,206,461, 2.7.40. Appl. 14.3.38. Deep-well pump.

K. P. Neilson. U.S.P. 2,206,466, 2.7.40. Appl. 29.2.36. Duplex pump for deep wells.

C. A. Combs. U.S.P. 2,206,835, 2.7.40. Appl. 27.11.37. Well-control equipment consisting of an inclined separating tank and a vortical tank connected to a well and to each other and a level controlling float in the vortical tank.

S. V. Dillon. U.S.P. 2,207,001, 9.7.40. Appl. 11.10.37. Well equipment consisting of an inflatable and deflatable packing and a source of pressure for such means.

G. R. Linville. U.S.P. 2,207,019, 9.7.40. Appl. 14.1.38. Combination packer.

H. R. Toney. U.S.P. 2,207,033, 9.7.40. Appl. 23.5.38. Apparatus for flowing wells.

C. S. Crikmer and R. A. Lamb. U.S.P. 2,207,118, 9.7.40. Appl. 7.7.38. Flow valve for wells.

W. R. Millican. U.S.P. 2,207,129, 9.7.40. Appl. 5.10.37. Flow valve for wells on gas-lift.

H. C. White. U.S.P. 2,207,184, 9.7.40. Appl. 29.9.37. Method of conditioning wells by using a foraminated body and later introducing reagents which attack this body and open its interstitial spaces.

J. A. Jesson and S. C. Kyle. U.S.P. 2,207,255, 9.7.40. Appl. 11.7.39. Casing-head for use on upper end of well casing enclosing a string of flow tubing terminating in a flanged tubing hanger.

J. M. Reynolds, W. M. Newton, and J. T. Lodbetter. U.S.P. 2,207,334, 9.7.40. Appl. 20.3.39. Method and apparatus for placing a filter body in a well.

P. H. Jones and A. L. Blount. U.S.P. 2,207,348, 9.7.40. Appl. 20.10.36. Determination of the connate water content of oil-producing formations by using a chemical tracer in the drilling fluid and analysing for it in the core.

E. J. Ashbrook. U.S.P. 2,207,448, 9.7.40. Appl. 13.8.37. Bottom-hole well plug which expands by means of a ratchet and pawls.

J. R. Yancey. U.S.P. 2,207,471, 9.7.40. Appl. 27.1.40. Casing-head with a relatively wide foundation ring.

J. R. Moser. U.S.P. 2,207,518, 9.7.40. Appl. 5.10.37. Pipe joint for surface pipes.

D. G. Hefley and J. B. Stone. U.S.P. 2,207,733, 16.7.40. Appl. 10.10.38. Treatment of wells with hydrochloric acid and a small quantity of oil.

H. A. Roimers. U.S.P. 2,207,750, 16.7.40. Appl. 10.8.38. Treatment of earth and rock formation with acid solution and then liquid silicate mixture which gels subsequently.

J. P. Neel. U.S.P. 2,207,937, 16.7.40. Appl. 15.11.38. Pumping-well hook-off device.

R. R. Kyner. U.S.P. 2,208,036, 16.7.40. Appl. 1.6.37. Well-flowing apparatus and method.

C. J. Somers. U.S.P. 2,208,087, 16.7.40. Appl. 6.11.39. Electric heater for oil wells to be inserted into casing.

J. O. McMillan. U.S.P. 2,208,193, 16.7.40. Appl. 10.12.36. Pneumatic displacement pump.

E. St. E. Kilby. U.S.P. 2,208,461, 16.7.40. Appl. 19.10.38. Pump piston.

J. G. M. López. U.S.P. 2,208,466, 16.7.40. Appl. 10.11.38. Gas and oil separator.

L. D. Mowrey. U.S.P. 2,208,468, 16.7.40. Appl. 15.7.38. Rod-line carrier.

W. F. Rurup. U.S.P. 2,208,775, 23.7.40. Appl. 9.5.39. Automatic by-pass valve for oil well-packer to permit passage of well fluid upward, and means with check valves to permit downward flow around this passage, but not in the opposite directions.

A. H. N.

### Hydrogenation.

**1300. Patents on Hydrogenation.** H. E. Potts. E.P. 523,649, 18.7.40. Appl. 18.10.38. Process for the destructive hydrogenation of carbonaceous materials containing solid matter in dispersion with hydrogen or gases containing hydrogen under high pressures and at high temperatures. A tube preheater is used having return bends in which interchangeable tube-like pieces are inserted constructed of or lined with alloys, or coated with high-melting enamels having a Brinell hardness of over 400.

J. C. Vlughter. U.S.P. 2,206,376, 2.7.40. Appl. 15.1.37. Process for non-destructive catalytic hydrogenation of olefins by passing vapours of olefinic hydrocarbons having a boiling point within the gasoline range and being formed by the polymerization of mono-olefins, together with water vapour and a gas containing free hydrogen, in contact with a hydrogenation catalyst.

H. B. M.

### Polymerization.

**1301. Patent on Polymerization.** Les Usines de Mello. E.P. 522,818, 27.6.40. Appl. 17.12.38. Process of olefin polymerization which consists in treating a gaseous olefin with a hot aqueous polymerizing reagent of a concentration of at least 50%. The conditions are such that only the dimer and small amounts of higher polymers are formed, and are removed from the polymerizing reagent as soon as they are formed as a predominantly dimer-water azeotropic mixture by azeotropic distillation.

H. B. M.

### Refining and Refinery Plant.

**1302.\* Treatment of Crude Oil from Tupungato at the Campana Refinery.** A. Piccioni. *Bol. Inform. Petroleras*, March 1940, XVII (187), 81-86.—This article describes the method of dealing with a shipment of crude oil of 36,300 m.<sup>3</sup>. A complete analysis is given of the crude oil and description of a topping plant with a Foster Wheeler furnace. Full particulars of the products and characteristics are provided. Particulars are also given of a coker still producing gas oil for cracking, and also details of a Cross cracking

plant and of the product obtained, and lastly the naphtha cracking plant. Finally the figures are given for the results obtained from each of the six processes employed.

H. I. L.

**1303.\* Fundamentals of Solvent-refining Operation.** E. W. Gard and E. G. Ragatz. *Oil Gas J.*, 6.6.40, 39 (4), 49.—The more important characteristics of an ideal solvent are: (1) high efficiency and selectivity for the quality of product desired; (2) high degree of stability; (3) ready gravity separation of its extract—raffinate phases; (4) residual traces left in the oil should have no deleterious effect; (5) ease of recovery; (6) non-corrosivity; (7) non-toxicity; (8) fluidity at atmospheric temperature; (9) cheapness. Correct evaluation of items 2–9 is straightforward, but item 1 is more difficult. It is accordingly considered in detail, the theoretical bases being contrasted with those of rectification. An experimental 12-stage continuous extraction unit, using benzol-SO<sub>2</sub> for the treatment of mixed base oils, has been used to evaluate the different factors involved. One series of tests provided data on the extent of increased yields with increased solvent ratios. Thus, when running to a 0.808-v.g.c. (87.5-v.i.) raffinate, increasing the solvent-oil ratio from 400% to 1060% increased the yield from 27% to 46%. The effect of varying the reboiling temperature indicates the necessity of proper manipulation of this stage in order to control solvent ratios. The importance of the point of entry of the incoming feed was shown by tests in a laboratory treater utilizing phenol and consisting of two 40-ft. treating columns instead of the alternate mixer-settlers of the previous SO<sub>2</sub> plant. Changing the inlet from the bottom of the second column to the top decreased the solvent requirement from 400% to 300% and gave a slightly higher yield of a slightly better-quality raffinate. Increasing the extraction temperature from 167–170° F. to 190–195° F. enabled the solvent ratio to be reduced from 375% to 300%. Further temperature increases would be possible, limited, of course, by the approach to the miscibility temperature. A comparison of phenol and benzol-SO<sub>2</sub> indicated that while similar solvent ratios were required for a 65-v.i. raffinate, 4½ times as much benzol-SO<sub>2</sub> as phenol was required for a 90-v.i. raffinate. Comparative yields for benzol-SO<sub>2</sub> to phenol were 0.93–1 for 65-v.i. raffinate and 0.60–1 for 90-v.i. raffinate. By plotting yield, solvent ratio, and raffinate quality data for these runs it is found that a substantially straight-line relationship exists between raffinate v.g.c. and volume per cent. raffinate for any given solvent ratio. At the lower end all solvents show a marked break in the slope, this break occurring at different v.g.c. values and different solvent ratios for different solvents. Thus for phenol treatment the break occurs at 92.5 v.i. and for SO<sub>2</sub> at 60 v.i. If, therefore, the operations are attempted below the solvents' break point, the solvent ratios required for a given yield efficiency will rapidly increase with relatively small increases in raffinate quality.

C. L. G.

**1304. Patents on Refining.** Standard Oil Development Corporation. E.P. 522,605, 21.6.40. Appl. 12.12.38. Treatment of mineral oil with selective solvents by distilling in a batch still, condensing the distillate obtained thereby into a number of consecutive fractions of narrow but progressively higher boiling range, and treating these fractions consecutively with a selective solvent.

E.I. Du Pont de Nemours. E.P. 523,451, 15.7.40. Appl. 29.12.38. Inhibition of deterioration of mineral hydrocarbons, etc., by incorporating therewith an arylidene amide obtained by condensing a polyamino with a proportion of an *ortho*-hydroxy-substituted aldehyde, which is aromatic in nature.

H. T. Bennett. U.S.P. 2,206,151, 2.7.40. Appl. 15.1.36. Method of avoiding thickening of the liquid oil during the process of sulphurizing fatty and mineral oils. This is achieved by heating a mixture of the liquid oil and sulphur in the presence of an aromatic amino-compound, maintaining the oil in liquid form during heating, and limiting time of operation, to prevent substantial thickening.

W. A. Schulze. U.S.P. 2,206,921, 9.7.40. Appl. 6.10.36. Method of sweetening gasoline stock containing organic sulphur compounds of the mercaptan type by contacting with a zirconium oxide catalyst. The mercaptans are converted into hydrogen sulphide, which is thereafter separated from the gasoline stock.

H. B. M.

## Analysis and Testing.

**1305. Analysis of Petrols. Physical & Physico-Chemical Methods.** — Abert. *Sci. et Ind.*, 1940, 290 bis (Supplement to *Revue Mécanique*), 53–60.—The methods discussed are: (1) the use of Verdot's law in the magnetic rotation of the plane of polarization of light; (2) use of the Gladstone–Dale and the Lorenz–Lorentz formulæ for specific refraction. These properties are highly constitutive, and give a clear distinction between the paraffins and naphthenes and the aromatic hydrocarbons, but they are of limited value, as they do not discriminate between the paraffins and naphthenes. These can be distinguished by: (3) critical solution temperature, (4) infra-red absorption; each hydrocarbon has its own series of absorption bands; thus, it is possible to distinguish between straight-chain and branched-chain paraffins, and hence between pro- and anti-knock paraffin hydrocarbons. This method has not, so far, been well developed, and is not accurate for quantitative investigations except for two component fractions. (5) Raman effect; each hydrocarbon possesses its own Raman frequencies, which are typical also of its homologues.

R. D. S.

## Motor Fuels.

**1306.\* Motor Fuels of the Present and Future.** G. Egloff. *J. Inst. Fuel*, June 1940, 13 (72), 175.—A comprehensive survey is presented of methods of production, properties, and fuel value of a series of petroleum, coal, synthetic, and other motor fuels and components. These include the following processes: distillation, thermal and catalytic reforming, thermal and catalytic cracking, production of polymer gasoline, *iso*-octane gasoline, catalytic dehydrogenation and thermal cracking of gaseous paraffins to produce olefines for further processing, alkylated gasolines (sulphuric acid and thermal processes), aviation safety fuels, compressed gases, and such fuels as ammonia, hydrogen, acetylene, and coal dust. Statistical data on the economic possibilities of the dehydrogenation process in conjunction with polymerization and *iso*-octane production and a note on the chemical structure of compounds in relation to their octane rating are also presented.

C. L. G.

**1307. Patents on Motor Fuel.** P. B. Onderdonk. U.S.P. 2,207,894, 16.7.40. Appl. 8.12.38. Preparation of an alcohol fuel of the nitrocellulose-gel type which has distributed therein a small amount of asbestos in the form of individual fine fibres. The latter are in sufficient quantity materially to reduce the irregularity of burning which would otherwise result from the presence of the nitrocellulose.

R. B. Rathbun. U.S.P. 2,208,105, 16.7.40. Appl. 28.8.37. Production of a stable motor fuel composed of a light-coloured gasoline stabilized by anthracene and lecithin, the amount of anthracene and lecithin not exceeding 15 lb./1000 brls. of fuel respectively.

T. B. McCulloch and J. E. Pollock. U.S.P. 2,209,204, 23.7.40. Appl. 11.3.38. Preparation of a motor fuel having a vapour pressure between  $6\frac{1}{2}$  and  $7\frac{1}{2}$  lb. Reid at 100° F. The fuel consists of substantial proportions of *isopentane*, *isopropyl ether*, and a branched-chain saturated paraffin containing at least 8 carbon atoms in the molecule blended to produce a fuel having 12–40% distilled Engler at 158° F.

H. B. M.

## Lubricants and Lubrication.

**1308.\* Piston-ring Coatings and their Effect on Ring and Bore Wear.** M. M. Roensch. *J. Soc. aut. Engrs*, 1940, 46 (5), 221–228.—Piston-ring scuffing most frequently occurs during the break-in period; it has been noticed for some time, and often leads to excessive bore and ring wear and high oil consumption. Methods of treating the surfaces of piston rings have been developed which aid in preventing scuffing during the break-in period. The coatings may be classified as chemical or metallic. The

chemical are: Ferrox, an iron oxide; Granoseal, an iron-manganese phosphate; Graphitox and Grafotox, a zinc-iron phosphate with colloidal graphite; and Surfido, ferrous sulphide. The metallic coating is electrolytically deposited tin.

The oxide coating consists of two layers, their total thickness being 0.0003 in. It is mildly abrasive, so that the ring itself polishes high spots from the bore; the softer outer layer permits rapid seating and the harder layer reduces the rate of wear. The phosphate coatings are softer than the raw iron, which gives them a quick initial seating and lapping action. These rings are capable of adsorbing and retaining considerable amounts of oil, which may help to prevent scuffing. The etched surface of Surfido-treated rings likewise acts as an oil reservoir, and the iron-sulphide coating has extreme-pressure characteristics. The metallic (tin) coating is soft and plastic, thus preventing localized pressure. All these coatings possess anti-welding properties.

The author has conducted rapid break-in tests which resulted in severe scuffing of untreated rings, but the treated rings withstood the same procedure with no signs of scuffing; these results are illustrated by numerous photographs. On road tests, coated rings showed 25% less wear, and field experience shows a marked reduction of oil-consumption complaints.

K. A.

**1309. Aviation Lubricants.** P. Lion. *Sci. et Ind.*, 1940, 290 bis (Supplement to *Revue Mécanique*), 67-76.—The extreme conditions in which an aircraft lubricant has to function demand an oil of the highest quality. The necessary properties are high viscosity index, high specific heat and thermal conductivity, high oiliness, low carbon value, low cold test, no corrosion of metals, and good oxidation characteristics. Formerly, castor oil was an ideal lubricant, but with the rapid advance in performance of the aero engine the conditions became much more severe than could be withstood by castor oil, and the use of mineral oils is practically exclusive. The French Air Ministry specified two grades of mineral aircraft engine lubricant: "heavy" and "medium heavy" defined by their viscosities in absolute units at 35° and 100° C. In addition, the ratio between the viscosities at the two temperatures were fixed, and flash point, cold test, and acidity were specified. A catalysed ageing test was carried out, after which viscosity increase and hard asphalt were measured. Other tests, non-standard, but often carried out and giving much useful information on behaviour are: specific heat, friction tests on the Woog and on the Charron machines, Conradson carbon residue, distillation, and interfacial tension with water. Examination of the oil after use is carried out with reference to the effect of the oil on the engine and vice versa; it includes measurement of the change of viscosity, acidity, carbon residue, and estimation of the content of diluent, ash, and products of oxidation. Correct interpretation of these sheds much light on the best lubricant for aeroplane engines. In order that such an oil be obtained, the properly selected crude must be subjected to careful distillation, after which the appropriate fraction undergoes deasphaltization, dowaxing, and filtration. Solvent refining is an advance which now enables the finest product to be obtained from the crude. Finally, oils thus refined can be still further improved by blending in special addition agents, chosen as the result of exhaustive tests, to depress the pour point, flatten the viscosity curve, or to inhibit oxidation or corrosion.

R. D. S.

**1310. Patents on Lubricants and Lubrication.** Standard Oil Development Corporation. E.P. 523,524, 16.7.40. Appl. 21.7.39. Improvements in blending agents for lubricating oils. The agents found to be most satisfactory fall within the class of alkyl- or aryl-substituted aromatic phosphite or thiophosphite esters which contain further substituent hydroxyl or mercapto groups attached directly to the aromatic nucleus.

E. W. Adams and G. M. McNulty. U.S.P. 2,206,245, 2.7.40. Appl. 10.6.36. Preparation of a lubricating composition consisting of a mineral lubricating oil and a small amount of an alkyl xanthic disulphide.

B. H. Lincoln, W. L. Steiner, and A. Henriksen. U.S.P. 2,206,573, 2.7.40. Appl. 16.9.38. Production of a lubricating composition consisting of a major proportion of hydrocarbon oil and a minor proportion of a halogenated alcohol.

C. F. Prutton, A. K. Smith, and H. E. Johnson. U.S.P. 2,208,161, 16.7.40. Appl. 19.10.39. Preparation of a lubricating composition consisting of a major proportion

of mineral oil, a relatively inactive organic sulphur compound, and a minor amount of an organic halogen compound.

H. P. Lankolma. U.S.P. 2,208,218, 16.7.40. Appl. 4.9.36. Improving a mineral oil capable of lubricating viscosity at high temperatures by incorporating therewith a small amount of a hydro-compound of the group consisting of hydroquinone, hydroquinidine, and hydrocinchomine. H. B. M.

## Gas, Diesel and Fuel Oils.

1311.\* **Mechanical Atomization of Fuel Oil Heavier than Bunker C.** G. C. Martinson. *Oil Gas J.*, 9.5.40, 38 (52), 80. (Paper before Fuels Division, A.S.M.E. Worcester, May 1940.)—The difficulties involved in the combustion of heavy cracking plant residues are discussed and a suitable type of burner is described.

The equipment in question consisted of boilers fitted with combination burners for oil and pulverized coal firing. When firing pulverized coal, the fuel is mixed with primary air at the pulverizers and delivered through the centro pipe of the burner assembly, whilst secondary air is forced through the air preheater by a forced draught fan and delivered to the burner assembly outside the pulverized coal pipe. For fuel oil only the secondary air supply is maintained. Difficulties were caused owing to the inadequate mixing of the fuel oil and air causing heavy coke deposits on the side-wall tubes. The oil flame failed to fill the throat, so that there was little mixing of the air and fuel, except at the outside of the oil flame cone. After a series of experiments with adjustable air vanes, selection was made of a mechanical atomizing burner tip developed for steel-mill purposes, which produced a wide angle of spray. It consisted of three atomizers set in a single burner head producing a flame cone angle of 120°. The burners can be withdrawn to a point at which the fire completely fills the throat without danger of infringement of the oil spray on the coal nozzle. Thus the atomized oil spray is forced into the secondary air stream, ensuring complete combustion with little excess air.

The burners have been in successful operation for 15 months, handling fuel of 800/1400 secs. S.F. at 122° F., operating costs comparing favourably with those given by pulverized coal. C. L. G.

1312. **Patents on Diesel Oil.** Standard Oil Development Corporation. E.P. 523,143, 5.7.40. Appl. 13.7.39. Manufacture of a compression-ignition fuel of the diesel type, consisting substantially of a hydrocarbon fuel to which has been added a small amount of an organic compound containing a thiocarboxylic acid radical. The latter imparts improved ignition qualities to the fuel.

Standard Oil Development Corporation. E.P. 523,522, 16.7.40. Appl. 21.4.39. Preparation of a compression-ignition fuel consisting of liquid hydrocarbons of the diesel fuel type and a small quantity of a soluble organo-metallic compound or organic salt of a metal selected from groups 2 and 5 of the Periodic System, and having an atomic weight above that of zinc.

H. G. Berger. U.S.P. 2,206,594, 2.7.40. Appl. 8.10.38. Preparation of an improved diesel fuel composed of a hydrocarbon fuel oil and a minor proportion of hydrogen persulphides and elementary sulphur in admixture therewith. H. B. M.

## Asphalt and Bitumen.

1313. **Preparation of Asphaltic Emulsions Obtained from the Petroleum at Comodoro Rivadavia.** S. Bortolotto. *Bol. Inform Petroleras*, March 1940, XVII (187), 78-80.—The asphaltic residuals obtained from low-pressure distillation of the petroleum, as well as those produced from blown mixtures with extracts of lubricating oils arising in the treatment of the latter with sulphur anhydride, are not easily emulsified. Particulars are given of the methods which have to be adopted in order to produce

stable emulsions. Tables are given with particulars and characteristics of an emulsion of blown asphalt and one of Bitalco. A further table is given containing the specifications for asphaltic emulsions laid down by the National Road Board. H. I. L.

1314. Patent on Asphalt. T. B. Wayne. U.S.P. 2,206,589, 2.7.40. Appl. 2.1.34. Method of resolving petroleum emulsions by subjecting them to the action of a water-wettable alkylated paracoumarone resin. H. B. M.

1315. Patent on Road Materials. J. R. Geigy A.-G. E.P. 523,025, 3.7.40. Appl. 22.12.38. Use of pulverized condensation product as a stiffener for road materials consisting of small stones and tar. The product is obtained by condensing with an aldehyde a pinewood pitch of substantial insolubility in petroleum hydrocarbons. It is added to the road-surfacing material before or during its laying. H. B. M.

### Special Products.

1316. Patents on Special Products. N.V. de Bataafsche Petroleum Maatschappij. E.P. 522,559, 20.6.40. Appl. 8.12.38. Separation of mercaptans from hydrocarbons with an aqueous solution of an alkali metal oxide containing a substantial amount of a mixture of an alkali metal alkyl phenolate and a sodium salt of a fatty acid having two carbon atoms in the molecule or a potassium salt of a fatty acid having one, two, or six carbon atoms in the molecule.

E.I. Du Pont de Nemours & Co. E.P. 522,643, 24.6.40. Appl. 16.12.38. Production of diethers of dimethylol urea by reacting substantially dry dimethylol urea and one or more normal, secondary, or isomonohydric alcohols at a raised temperature in the presence of anhydrous magnesium sulphate.

E.I. Du Pont de Nemours & Co. E.P. 522,644, 24.6.40. Appl. 16.12.38. Preparation of an ether of a methylol urea by reacting water-wet methylol urea with a monohydric alcohol in the presence of an acid catalyst and neutralizing the acid catalyst after substantial completion of the reaction.

Society of Chemical Industry in Basle. E.P. 522,658, 24.6.40. Appl. 19.12.38. Manufacture of nitrogenous naphthalene derivatives by causing a halogenated naphthalene which contains at least two halogen atoms, at least one of which is in a  $\beta$ -position, to react with a compound which contains at least one hydrogen atom attached to a nitrogen and contains the radical of a compound capable of being vatted.

Howard and Sons. E.P. 522,729, 26.6.40. Appl. 30.9.38. Manufacture of mannitol by subjecting fructose to catalytic hydrogenation in the presence of an added organic polyhydroxy compound and isolating mannitol from the product of hydrogenation.

I.G. Farbenindustrie A.-G. E.P. 522,835, 28.6.40. Appl. 19.12.38. Manufacture of trichloroacetonitrile by chlorinating acetonitrile while exposing it to a source of light and to a temperature of 50–80° C.

E.I. Du Pont de Nemours. E.P. 522,840, 28.6.40. Appl. 19.12.38. Process for the manufacture of secondary alkyl monosulphonic acids or salts thereof.

J. D. Riedel and E. de Haen A.-G. E.P. 523,047, 4.7.40. Appl. 28.10.37. Process for the preparation of a trisubstituted barbituric acid.

H. Gudgeon and R. Hill. E.P. 523,080, 4.7.40. Appl. 20.12.39. Manufacture of 1-carbalkoxy- and -carbalkoxyalkoxy-butadienes-1:3 by heating alkyl or alkoxy-alkyl  $\alpha$ -acyloxy- $\beta$ -ethylidene propionates in gaseous or vapour form at a temperature between 330° and 600° C.

Standard Oil Development Corporation. E.P. 523,248, 10.7.40. Appl. 31.10.38. Preparation of solid copolymers of isobutylene and butadiene by reaching 50–90% by

weight of isobutylene with 5-50% by weight of a butadiene at a temperature below  $-50^{\circ}\text{C}$ . in the presence of a catalyst consisting of an aluminium chloride-ethyl chloride complex.

Society of Chemical Industry in Basle. E.P. 523,396, 15.7.40. Appl. 3.10.38. Manufacture and application of ether and ester condensation products.

Society of Chemical Industry in Basle. E.P. 523,448, 15.7.40. Appl. 29.12.38. Manufacture of melamine from melam by heating the latter in a closed vessel at a temperature above  $150^{\circ}\text{C}$ . with anhydrous ammonia.

R. Greenhalgh. E.P. 523,466, 15.7.40. Appl. 30.12.38. Manufacture of mono-hydroxyalkylamides of higher fatty acids by the interaction of a methyl or ethyl ester or a glyceride of a higher fatty acid and a monohydroxyalkylamine having 2, 3, or 4 carbon atoms.

J. R. Geigy A.-G. E.P. 523,496, 16.7.40. Appl. 9.1.39. Improvement in the manufacture of condensation products from isatin derivatives and phenols. 1 mol. of an *N*-benzylated isatinsulphonic acid is condensed with about 2 mols. of a phenol or homologue thereof or of an ether of such a phenol or homologue.

Standard Oil Development Corporation. E.P. 523,520, 16.7.40. Appl. 16.3.39. Preparation of an emulsion consisting of a mineral oil, a water-soluble salt of an *iso*-butyl phenol sulphonic acid, and oil-soluble salts of the sulphonic acid compounds obtained by the treatment of petroleum oils with strong sulphuric acid.

F. W. Kirkbride. E.P. 523,555, 17.7.40. Appl. 4.1.39. Oxidation of trichlorethylene by treatment with gaseous oxygen. The trichlorethylene is exposed to actinic radiation up to the stage wherein the reaction liquor has acquired an acid value of 3N and preferably between 15 and 20N. Subsequent oxidation is carried out at a temperature above  $50^{\circ}\text{C}$ .

British Celanese, Ltd. E.P. 523,635, 18.7.40. Appl. 11.1.39. Conversion of alkyl alcohols into polymerizable alkyl esters of unsaturated acids by oxidizing the alkyl alcohol to the corresponding unsaturated aldehyde, treating the aldehyde with a concentrated alkali solution, and converting the alkali salt thus produced into an ester by treating with an alkyl ester of an inorganic acid.

Armour and Co. E.P. 523,705, 19.7.40. Appl. 17.2.39. Preparation of a naphthalene containing as a plasticizer an amide of the general formula  $RCONHR'$ , wherein *R* is an alkyl radical containing at least nine carbon atoms, and *R'* is hydrogen, an aromatic or aliphatic hydrocarbon radical, or an aliphatic acyl radical.

H. B. Hass. U.S.P. 2,206,813, 2.7.40. Appl. 31.8.36. Production of nitrohydrocarbons by chemically combining. Substantially pure nitrogen dioxide and a saturated hydrocarbon containing more than 2 carbon atoms are contacted wholly in the vapour phase at a temperature of  $300-600^{\circ}\text{C}$ .

J. M. Weiss. U.S.P. 2,206,377, 2.7.40. Appl. 6.8.37. Production of maleic acid from benzene by passing benzene and air over a heated contact mass having a productive catalytic agent.

J. W. Putt. U.S.P. 2,207,552, 9.7.40. Appl. 8.12.36. Production of aromatic hydrocarbons and diluents and solvents of a predominantly aromatic hydrocarbon content the dilution ratio, kauri butanol, and dimethyl sulphate value of which closely approach or equal those of coal-tar aromatic hydrocarbons produced by the pyrolysis of coal.

W. E. Currie. U.S.P. 2,209,190, 23.7.40. Appl. 11.1.36. Manufacture of hydrocarbons from carbon oxides by subjecting a mixture of an oxide of carbon and hydrogen to the action of a Fischer-Tropsch catalyst at temperatures between  $380^{\circ}$  and  $450^{\circ}\text{C}$ . and at a total pressure between 10 and 20 atmospheres, but in the presence of sufficient diluting gas to ensure a partial pressure of combined reactants below 5 atmospheres.

H. B. M.



## Detonation and Engines.

1317.\* **Economic Aspects of Light Airplane Engines.** C. T. Doman. *J. Soc. aut. Engrs.*, 1940, 47 (1), 284-290.—The author's organization has developed a basic design of 4-cyl. horizontally opposed air-cooled engine which is used both for commercial vehicle and light aircraft applications. Whilst there are numerous detail differences, the similarity of parts permits the use of the same production fixtures, with consequent reduction in cost of the aircraft unit. Both models use 73-octane fuel. The commercial engine develops 45 b.h.p. with 5.5 : 1 compression ratio; the aircraft engine 55 b.h.p. at 6.6 : 1. A description is also given of a 4-cyl. opposed engine developing 80 b.h.p. with 73-octane fuel.

K. A.

## Coal and Shale.

1318. **Patent on Coal.** J. Jannok. U.S.P. 2,208,514, 16.7.40. Appl. 11.9.37. Production of pulverulent motor fuel for coal-dust motors by treating solid extracts of coal with oxides of nitrogen in such a way that the initial material retains its loose pulverulent condition, and nitrogen and oxygen are incorporated with the coal extract.

H. B. M.

## Economics and Statistics.

1319.\* **Economics of Liquefied Petroleum Gases.** J. W. Vaiden. *Oil Gas J.*, 23.5.40, 39 (2), 74. (N.G.A.A. paper Tulsa, May 1940.)

The economics of the utilization of propane and butane as domestic fuel, in central gas plants, as fuel for I.C. engines or as a blending agent and in polymerization and related processes is discussed. Conclusions reached are:—

(1) Extraction of propane and butane beyond the limits incidental to efficient recovery of natural gasoline is likely to prove uneconomical, it being calculated that the cost of the equipment necessary to recover 95% of the butanes amounts to \$4/\$15 per gallon of gasoline recovered (depending on the butane content).

(2) The extension of the marketing of propane as domestic fuel offers small possibilities of profit, owing to heavy investments necessary, increased competition, and expensive distribution costs in those sparsely populated areas where a market still remains.

(3) Butane is more economical to distribute, owing to the lower pressure and lighter containers used. Its use as domestic fuel has not been as highly developed as that of propane, but present supplies of butane are more than sufficient for this purpose, so that its future value will depend more on the demand for other purposes.

(4) The extension of the use of propane or butane in central gas plants offers possibilities, particularly for communal or private plants for the generation of electricity, operation of water and sewage pumps and refrigeration plants.

(5) The use of butane and/or propane as fuel for I.C. engines for farm machinery, trucks, and buses is well developed, and is now spreading into the oil-fields for drilling equipment. An increase in horse power of more than 56% with a 9.95 compression ratio using propane fuel or 19.3% with a 6.75 compression ratio using butane is shown over a 61 O.N. gasoline at a 4.33 : 1 compression ratio. Fuel savings of 30.9% have been shown with these gaseous fuels. No advantage is given unless the compression ratio is increased.

(6) It was calculated in 1934 that the incorporation of 5% of butane in motor fuel would save the industry \$55,000,000 per annum, chiefly due to lowering of crude oil requirements and saving of tetraethyl lead.

(7) Liquefied gases available in refineries near large centres of consumption offer competition with natural gasoline plants located at some distance from the point of distribution. The greater use of these gases for polymerization or alkylation would reduce this competition. At present these processes can only be considered in connection with refinery operations, since natural gas requires expensive cracking equipment to produce the necessary basic products, and, in addition, refineries possess the

necessary blending materials. Diversion of propene and butene from gasoline to polymerization plants will require the purchasing of additional quantities of butane. Its value as gasoline is estimated at 6 cents per gallon or as fuel at 0.7 cent per gallon, so that if half of the available butane-butene is used for each purpose, it can be replaced by butane for which as high as 3.35 cents per gallon can be paid. Alternatively, natural gasoline containing, say, 30% butane may be used to obtain the necessary volatility.

C. L. G.

## BOOK REVIEWS.

**Physical Constants of Hydrocarbons. Volume 2. Cyclanes, Cyclenes, Cyclynes, and Other Alicyclic Hydrocarbons.** By Gustav Egloff. Pp. 605. Reinhold Publishing Corp., New York, or Chapman & Hall, London. Price 72s.

On the occasion of the publication of Volume 1 of this series early in 1939, a reviewer wrote, "When the Universal Oil Products Co. publish a work composed entirely of data, statistics, and bibliography, petroleum chemists are assured without the recommendation of a reviewer that no organization is better fitted to compile such a book, so high is the reputation in the petroleum world of the Records and Filing Department of this Company."

That this opinion was whole-heartedly endorsed by petroleum chemists is evident from the widespread success of Volume 1, and there is no doubt that Volume 2 will achieve an equally appreciative reception.

The present volume follows the same system as the first—that is to say, it embodies all the available data on the principal physical constants of the hydrocarbons—namely, melting point, boiling point at various pressures, specific gravity and refractive index, each entry bearing the reference to the source of information. That novel and very valuable feature of Volume 1, the indication as to which of the data is considered the most reliable, has been retained.

Volume 2 deals with the alicyclic hydrocarbons (excluding the aromatic series) and covers the cyclanes, cyclenes and di-, tri- and tetra-enes, cyclynes (acetylenic types), spiro-hydrocarbons, and "hydrocarbons of known but unclassified structure," some of which, such as the carotenes, are of extreme complexity. Lastly, there is a miscellany of hydrocarbons of unknown structure and frequently fanciful names. Many of these are sesquiterpenes deriving their names from their natural origin.

In compiling this volume Dr. Egloff has had a much more difficult task in many ways than he had in the previous volume. The alicyclic compounds in the first place have received on the whole much less attention from chemists than the open-chain hydrocarbons, so that data are fewer and less reliable. Geometrical isomerism is a much more complicated phenomenon with cyclic hydrocarbons than with open-chain olefines, and in all but a few cases the spatial structure of the hydrocarbons described is entirely unknown, although very considerable alternative configurations are possible. Even nomenclature is confused. Chemists frequently term these hydrocarbons polymethylenes, naphthenes, and in some cases hydroaromatics and terpenes, as well as cyclanes (or -enes) and *cycloalkanes*. Dr. Egloff's first and probably most difficult task was to decide on his system of nomenclature, which was required to cover an extraordinarily wide range of hydrocarbon types. He decided to base his system on the Geneva International Rules, though certain adaptations and amplifications proved necessary. This leads to some very formidable and complicated terminology, especially in the bicyclic terpene series. However, Geneva terminology is at any rate consistent, and can with practice (we suppose) be learned, so we must admit that Dr. Egloff has succeeded in a task which would daunt most chemists.

Petroleum chemists will not find as much in this volume as in the last of direct interest to them, for whereas the open-chain paraffins and olefines are met with at every turn in modern petroleum chemistry, the naphthenes so far have been a field little known, and not extensively employed in synthetic operations. Interest, however, has turned to cyclization, so that naphthenes are not likely to remain in the semi-unexplored territory they have hitherto occupied.

We can, therefore, repeat in all sincerity that this volume, like its predecessor, is one that all petroleum research laboratories should possess for purposes of reference, even though the rather formidable price of 72s. may cause hesitation.

F. B. THOLE.

**Industrial Plastics.** By Herbert R. Simonds. Pp. xii + 371. Sir Isaac Pitman & Sons, Ltd., London. Price 22s. 6d.

This volume, in spite of the wide scope of its title, makes no claim to be a general treatise on the chemistry, properties, or technology of plastic substances. Although there is a real need for a book covering modern aspects of the production and fabrication of moulding powders and plastic articles, the present volume can only in part be considered as filling this gap. Mr. Simonds is concerned mainly with a very general description of the properties of the more common synthetic resins and American practice in their use. The general arrangement is, however, rather confused and insufficiently concise, and there is a great deal of repetition of material, notably in Chapters I, II, III, VI, and IX. The text is, moreover, rather marred by long and tedious lists of common articles, from ping-pong balls to starchless collars normally fabricated from the various synthetic resins, while the "slick" American prose makes odd reading to British ears in a technical work.

Chapters I and II dealing mainly with the classification of plastics and their basic raw materials are perhaps the least satisfactory, and the author overcomes the well-known difficulty of classifying these materials by merely quoting a number of rival systems, one of which is worthy of reproduction here :

"(1) Animal (casein), (2) vegetable (cellulose), (3) mineral (phenolics), (4) air (nitrates-ureas)."

Chapter III—"Ten Important Plastics"—deals reasonably adequately, but in very general terms, with the production and properties of the common synthetic resins, but no attempt is made to deal with chemical and physical properties in detail or with the production of the moulding powders in the chemical aspects.

The next five chapters cover a good general account of moulding, casting, and laminating technique and practice, including mould design and fabrication, but a more detailed discussion of injection moulding practice would here be advantageous. These chapters are copiously illustrated by excellent photographs of moulding equipment, etc., and of moulded plastics.

Chapter X deals all too briefly with the natural resins and waxes, rubber and the alky resins, whilst Chapter XI gives a very useful account of the fundamentals of the design of plastic articles.

Chapter XV attempts in very small compass to deal with the structural chemistry of the common synthetic resins and to distinguish between the properties of molecules with two- and three-dimensional linkages in terms presumably intelligible to the layman—here there are an undesirable number of errors in the formulæ.

While the author's enthusiasm makes excellent propaganda for the extended use of plastics, it is difficult to recommend this book to any specific class of reader. It should, however, prove useful to one desiring a *résumé* of the properties of synthetic resins in relation to methods of processing them, to the user and potential user of moulding powders desiring to appreciate the full range of products and methods now available, and perhaps to the student in conjunction with a more scientifically based text.

E. W. M. FAWCETT.

**This Fascinating Oil Business.** By Max W. Ball. Pp. 444. Bobbs-Merrill Co., New York.

This book equally well deserves the adjective fascinating. It is well printed on good paper, of a convenient size, of reasonable price and good value for the money. The author is well qualified to write on the subject, having been associated with the industry in various capacities for thirty years. His experience with the U.S. Geological Survey, with the U.S. Bureau of Mines, and with two major oil companies, and his connection with scientific and technical societies have obviously given him a remarkable knowledge of all branches of the industry. This rather rare combination, together with an easy and attractive style, has enabled him to produce a remarkable book.

The book is offered "to eager-minded people as a journey of discovery." It will be equally pleasing and interesting to people who are engaged in one or more branches of the industry, who wish to have some knowledge of its other branches explained in a simple but accurate manner. A wise start is made by

some definitions and usages which are important, as many words in the oil jargon are used in special senses. The second chapter is unusual; it gives the reader short introductions to the oil-men, lease-men, pipe-liners, toolpushers, shooters, promoters, and salesmen. The chapter on oil geology is clear, up to date, and well illustrated by good diagrams. Geophysics is well handled and the information given re the latest methods is right up to date. This is followed by a most interesting chapter on "Acquiring the Right to Drill," unusual in a book which is mainly technical. Two chapters are devoted to drilling, including all the associated operations of acidizing, mudding, fishing, coring, and others. This chapter is well illustrated.

A concise chapter deals with the principles of producing, explaining water and gas pressures, gas-oil ratios, and decline curves, as well as proration and potential production. This is followed by one on the mechanics of this subject, which deals also with such problems as the life of a field, cost of production and mining oil sands, with special reference to Pechelbrom and Alberta.

The chapter on transportation deals well with pipe-lines and tank wagons, but dismisses the important subject of tankers with a picture and a few words.

The simple chemistry and physics of refining are treated clearly, but in an elementary way. The necessary points in specifications for various products are clearly explained, but the treatment is in some cases even too elementary, assuming that the reader knows nothing of elementary science. Only twenty pages are devoted to the refinery operations; the subject is, however, well condensed, and all the important operations are mentioned. "Most refineries have a pungent and pervasive odour that only refiners appreciate. If you would like to fill your lungs with unpolluted air suppose we take to the open road and watch the marketing of the products we have made."

The vastness of the distributing in comparison with the producing and refining industries is emphasized, but this is well condensed into the confines of one chapter. This chapter is very far from being a mere description of the methods of distributing, as it deals with such interesting subjects as prices, competition, service and sales efficiency, and the law of supply and demand.

The remaining third of the book deals with research and future possibilities; the historical development of the industry in the Old and New Worlds; and oil and the war. These chapters are well written, and contain a vast amount of interesting and accurate information, and provide very interesting reading.

The last chapter—"Oil and the War"—is necessarily now out of date.

The book is not written for oil-men, but for those who wish to get a clear and interesting picture of the industry as a whole. This picture is well presented in a brisk style. Most of the examples are taken from American practice. There are a few mistakes and inconsistencies, but they are not of importance. The official A.P.I. spelling of kerosine is not adopted. The view that oil is produced by slow distillation is not generally held, "aluminum" is hardly strange to English readers, but "busses" is. There are a few misprints, mainly in place names. The index is full and good.

The book is certainly worthy of a place in the libraries of all those who are engaged in any section of the industry and take an interest in others or in the industry as a whole.

J. KEWLEY.

**Conversion of Petroleum. Production of Motor Fuels by Thermal and Catalytic Processes.** By A. N. Sachanen, D.Sc. Pp. 413. Reinhold Publishing Corporation, 330 West Forty-Second Street, N.Y., 1940. Price 38s.

The scope of this comprehensive treatise can best be gauged by listing the headings of the chapters, which are as follows:—

- Chapter 1: Thermal and Catalytic Reactions of Hydrocarbons.
- „ 2: Fundamental Factors of Cracking.
- „ 3: Fundamental Factors of Hydrogenation.
- „ 4: Cracking Equipment.
- „ 5: Cracked Gasoline.
- „ 6: Treatment of Cracked Gasolines.
- „ 7: Cracked Products other than Gasoline.

As may be expected from one of the authors of *Chemistry and Technology of Cracking*, the subjects are very fully dealt with. Almost 400 references from published literature are given, many of them from articles published in 1939, so that the volume is clearly up to date, and no important aspect of the subjects has been neglected.

Interesting comments are made on the Houdry System of Cracking, but the main value of the book lies in the bringing together in one volume of such a large number of extracts from the literature which is so largely published by monthly journals.

A few errors caught the reviewer's eye, such as on page 241, where a heat transfer of "15000 to 20000 B.T.U. per square inch" is clearly in error for that quantity per square foot.

The definition of "cracking" on page 103 appears to be unnecessarily rigid—i.e., the treatment of petroleum products at temperatures higher than 400° C., for the decomposition of these bodies with aluminium chloride at 200–250° C. referred to on page 143 is undoubtedly a cracking reaction.

In Table 90, page 194, a definition is needed in the last column referring to yield, and the reviewer questions the soundness of the reasoning at the end of paragraph 3, page 246, regarding vapour locking of a hot oil pump.

The diagrams are mainly of good quality, and in most cases the description of the diagram is on the page facing it.

These criticisms are, however, minor when contrasted with the vast amount of information contained in the volume.

W. N. HOYTE.

## BOOKS RECEIVED.

**Medical Manual of Chemical Warfare. 1939. Supplement. Arseniuretted Hydrogen Poisoning.** Pp. 7. H.M. Stationery Office. Price 2d. net.

This pamphlet gives an account of the general properties and detection of arseniuretted hydrogen, together with a detailed description of the symptoms, pathology, and treatment of poisoning by this gas. The most characteristic feature of its action is the destruction of the red-blood corpuscles, with the consequent appearance of hæmoglobin in the urine and the development of jaundice and anæmia. The kidney and liver are also directly affected by the absorbed arsenic. Exposure for a few minutes to a high concentration of arseniuretted hydrogen may be rapidly fatal.

**Transactions of the Institution of Chemical Engineers. Vol. 17, 1939.** Pp. 201. Institution of Chemical Engineers, 56, Victoria Street, Westminster, London, S.W.1.

Among the ten papers presented before the Institution during the past year, the following may be mentioned as being of particular interest to the Petroleum Industry:

*Problems of Compressors and Compressed Gases in Industry.* (R. L. Quartier.)

*Heat Transmission in Evaporative Condensers.* (A. K. G. Thomson.)

*The Theory of Gas Compression and Circulation.* (Prof. D. M. Newitt.)

*Some Aspects of Fundamental Research on the Corrosion of Metals.* (W. H. J. Vernon.)

**The Journal of the Iron and Steel Institute. Vol. CXXI, No. 1, 1940.** Proceedings, xiv + 1 p–458 p; Abstracts and Bibliography, 1 a–321 a; Indexes, 1–61. Iron and Steel Institute, 4 Grosvenor Gardens, London.

This volume contains nine papers presented at the Annual General Meeting held in London on May 2nd and 3rd, 1940, together with discussions and correspondence on them. The volume, as in preceding years, is divided into two sections. Section 1 opens with the Minutes of Proceedings, including the speeches made at the Members'

Luncheon, the Report of Council and Statement of Accounts for 1939, and the papers enumerated above. Section II is devoted to a survey of literature on the manufacture and properties of iron and steel and kindred subjects.

**Transactions of the Institute of Marine Engineers. Vol. 51. Session 1939-1940. Pp. 397.** Published by the Institute, London.

Sixteen papers read before the Institute during the 1939-1940 Session are reproduced, including two on diesel installations, viz. :—

*Some Recent Installations and their Characteristics.* (C. C. Pounder.)

*The Origin and Development of the Heavy-Oil Engine.* (Akroyd Stuart.)

# INSTITUTE NOTES.

SEPTEMBER, 1940.

## STUDENTS' MEDAL AND PRIZE.

The Council has awarded the Students' Medal and Prize to Mr. T. Y. Ju, Stud.Inst.Pet. (Birmingham University), for an essay on "Behaviour of Fuels in C.I. Engines."

A Special Prize has also been awarded to Mr. D. G. Brunner, Stud.Inst.Pet. (Birmingham University), for an essay on "Mud Fluids for Drilling."

B. A. Murphy (Melbourne) and P. G. Owen (Birmingham University) have been highly commended for their essays.

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## NEW MEMBERS.

The following elections have been made by the Council in accordance with the By-Laws, Section IV, Para. 7.

Elections are subject to confirmation in accordance with the By-Laws, Section IV, paras. 9 and 10.

### *As Fellows.*

BROWN, Norman Fraser	...	...	...	Burma.
KUHN, Wayne Edward	...	...	...	New York.
PRUTON, Carl F.	...	...	...	Cleveland, Ohio.
SMITH, Roland Wilfred John	...	...	...	Shell Haven.
SUTER, Hans H.	...	...	...	Trinidad.

### *Transfer to Fellows.*

HUNTER, Thomas Girvan	...	...	...	Birmingham.
KEIGHTLEY, Walter Allison	...	...	...	London.
LEWIS, Robert Iltyd	...	...	...	Teddington.

### *As Members.*

ALLEN, Eric Edgerton	...	...	...	Anglesey.
ALLEN, Sydney Hugh	...	...	...	Leeds.
MILLS, Leonard	...	...	...	Ormskirk.
MOON, Alec	...	...	...	Pinner.
MOORE, Lancelot Frederick	...	...	...	East Moseley.
SMITH, James Edward	...	...	...	Trinidad.
STOTT, Victor Howard	...	...	...	Manchester.
THOMPSON, John Rennet	...	...	...	Manchester.
TULLY, James	...	...	...	Thropton (Northumberland).
YONGE, Dudley Arthur	...	...	...	Chester.

### *Transfer to Member.*

COOPER, Arundel David	...	...	...	Egypt.
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### *As Associate Members.*

AGOSTINI, Pierre Leon	...	...	...	Trinidad.
GIBBS, Eric Clarence	...	...	...	London.
PEASE, Sherman Levi	...	...	...	Minneapolis.
PINDER, John Cuthbert	...	...	...	Nottingham.
ROUGHEDGE, Norman Donovan	...	...	...	Sunderland.
SIMPSON, Michael John	...	...	...	Teddington.

### *Transfer to Associate Members.*

HAWORTH, Alfred John	...	...	...	Burma.
PACHACHI, Nadim	...	...	...	Iraq.

### *As Student.*

PYMAN, Lawrence Lee	...	...	...	Cranwell.
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## CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

- BAARS, Gerrit., Chemical Engineer, c/o Mrs. Bailey, Edgerton House, Great Sutton, Wirral. (*J. A. Oriol ; H. LeQ. Herbert.*)
- BUSH, Sydney Steve, Technical Representative (*Shell-Mex & B.P., Ltd.*), 41, Weymouth Avenue, Ealing, W.5. (*A. E. Hope ; F. N. Harrap.*)
- DAVIDSON, Anthony Dryden, B.Sc., Chemical Engineer, c/o Foster Wheeler, Ltd., Aldwych House, Aldwych, London, W.C. 2. (*A. W. Nash ; R. K. Fischer.*)
- FLETCHER, Charles Horace, Mechanical Engr. and Driller, A.T.M.N., Ltd., P.O., Barakin Ladi, Northern Nigeria, W.A.
- HOLE, Herbert Wray, General Manager, New Brunswick Gas & Oil Fields, Canada. (*C. A. P. Southwell ; A. E. Dunstan.*) (*Trans. to Fellow.*)
- HUBLEY, John Stuart, B.Sc., Refinery Operator, Trinidad Leaseholds, Ltd., Pointe-a-Pierre, Trinidad, B.W.I. (*B. G. Banks ; J. T. T. Robinson.*)
- JOHNSTON, Douglas Gordon, Lubrication Engr. (*The Texas Oil Co.*), 185, Welling Way, Welling, Kent. (*N. L. Anfilogoff ; W. A. Webster.*)
- KEACH, Raymond Harry, B.Sc., Chemical Engr., Foster Wheeler, Ltd., Aldwych House, London, W.C. 2. (*A. W. Nash ; R. K. Fischer.*) (*Trans. to A.M.*)
- LANGDON, Charles Ernest James, B.Sc., Chemist, 32, Moor Mead Road, Twickenham, Middx. (*Dr. Dunstan ; D. A. Howes.*)
- LE BLANC-SMITH, William Leonard, Technical Representative (*Vigzol Oil Refining Co.*), "Walnut Tree Cottage," Great Barton, Nr. Bury St. Edmunds, Suffolk. (*S. Elliman ; L. Mills.*)
- MARGOSCHES, Charles G., Ing.-Dr., Research Chemist, 113, Hubert Grove, London, S.W. 9. (*M. L. Steinschneider ; L. Singer.*)
- RALPH, Noël Albert, Works Chemist (*Horton Manufacturing Co.*), 7, Frankland Close, Croxley Green, Herts.
- WARD, Stanley Allen, B.Sc., A.I.C., Chemical Engr. (*Foster Wheeler, Ltd.*), "Tresco," 7, Seaforth Gardens, Stoneleigh, Ewell, Surrey. (*R. K. Fischer ; W. H. Hoyte.*)

ARTHUR W. EASTLAKE,

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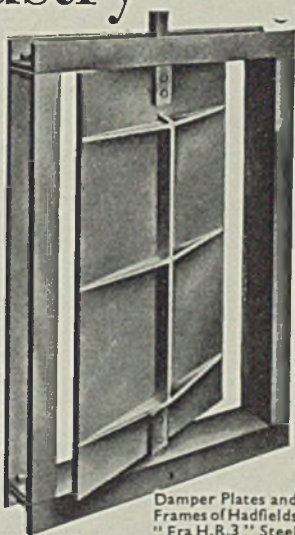


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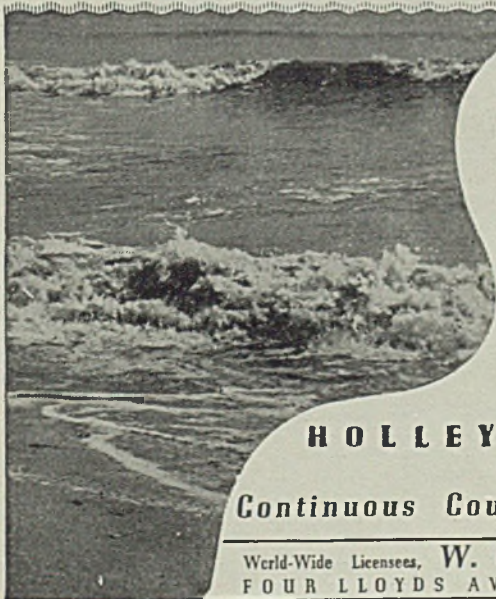
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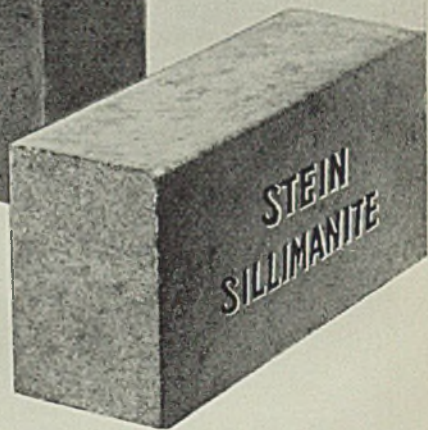
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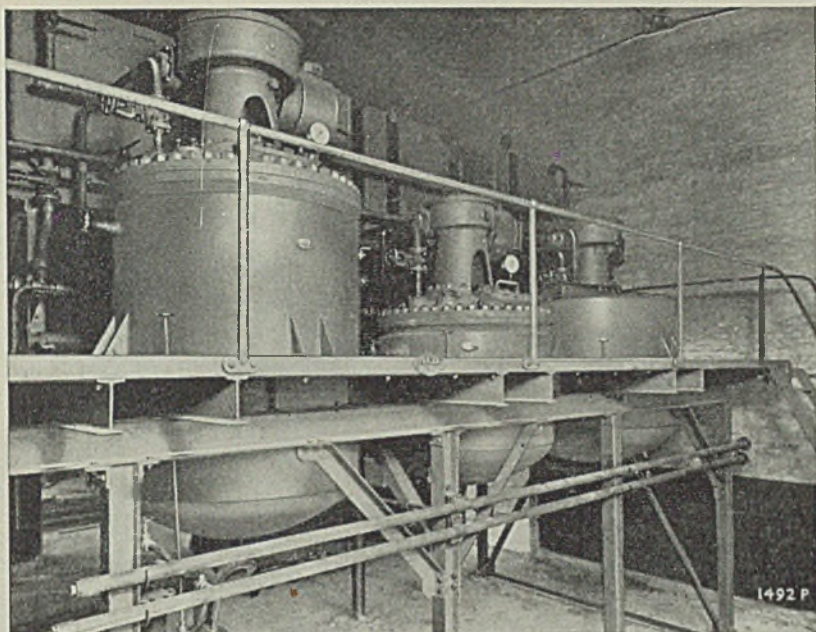
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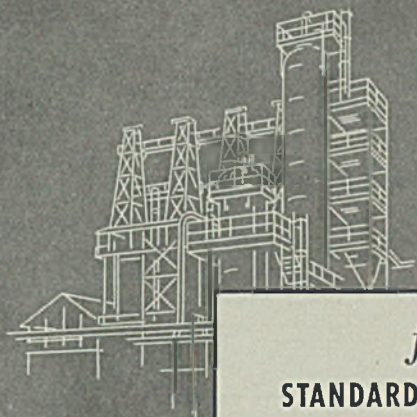
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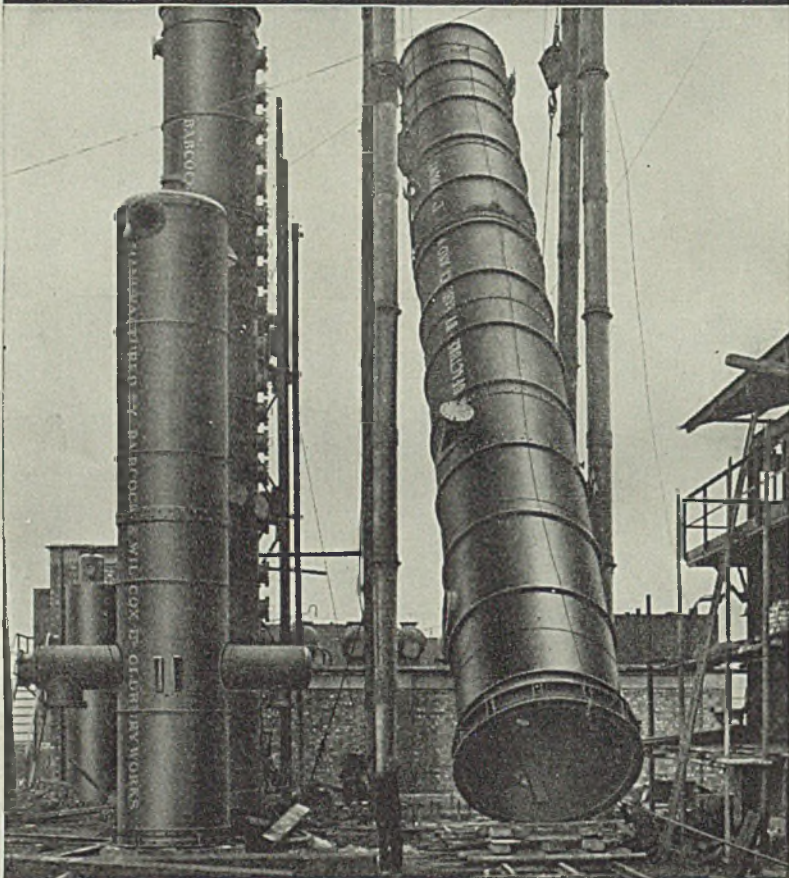
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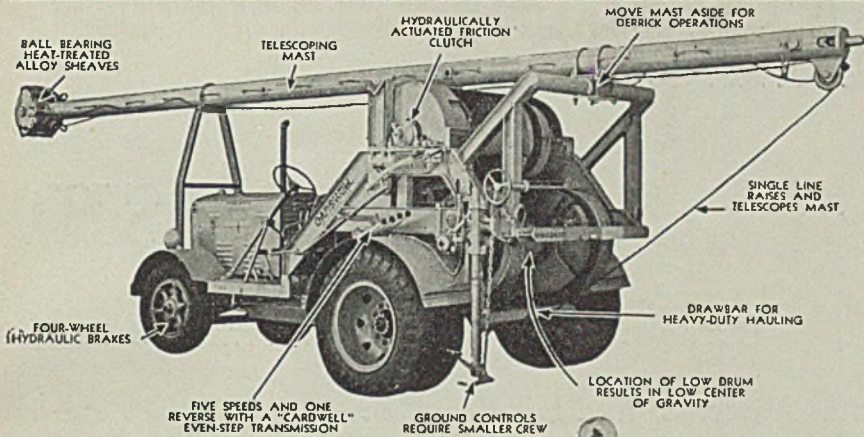
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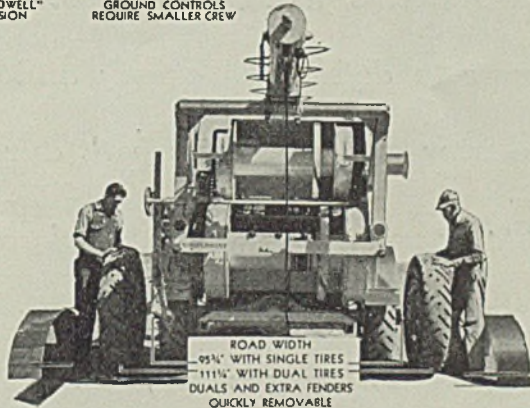
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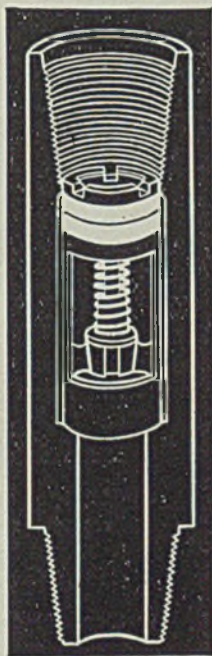
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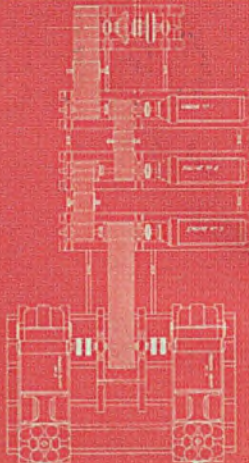
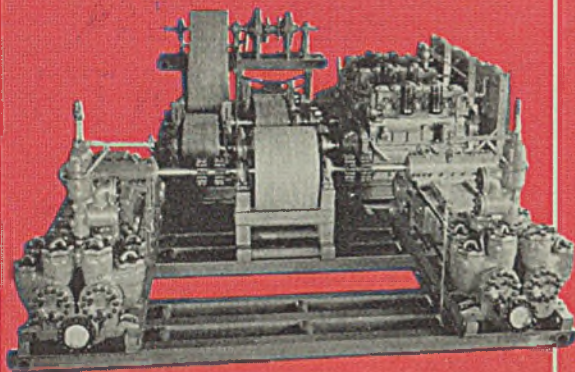
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