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THE SOLVENT EXTRACTION OF LUBRICATING OILS.*

By H. TER MEULEN.

THE first solvent-extraction plant in the oil industry operated according to the Edeleanu process, and treated kerosine with liquid sulphur dioxide. In view of the great success obtained with this process, an extensive research in this field was started, and the theory of the extraction with solvents developed mainly in the direction of kerosine treating. When the industrial development of the lubricating oils proceeded so far that the natural supply of high-grade oils was insufficient to meet the demand, and solvent extraction showed itself to be able to produce high-grade oils from base materials which, until then, had supplied only second-grade lubricating oils, it was obvious that the process, together with the theory of the extraction process, was applied for lubricating-oil treating. The well-known triangle for the graphical interpretation of ternary systems was also used to explain the phenomena encountered in the lubricating-oil field. It was soon realized, however, that the extraction of lubricating-oils involved many more factors than the extraction of kerosine, and an endeavour was made to overcome these difficulties by various assumptions regarding the base composition of the lubricating oils.

The main difference between kerosine and lubricating-oil composition is the fact that the former consists of two or three groups of components, the paraffins, naphthenes, and aromatics, which in each group can be considered to react as a single compound. In the lubricating oils all the components can also be classified in these three groups, but the components of one group are so widely different in composition that they do not act similarly when treated with a solvent. This is due to the fact that there are so many combinations of paraffins with aromatics and naphthenes and *vice versa* that it is almost impossible to classify these combination molecules in a certain group.

This difference between kerosine and lubricating-oil extraction demonstrates itself immediately when we consider the methods by which these two processes are controlled. Kerosine-extraction processes are controlled by methods based on the chemical differences between raffinate and extract, such as percentage aromatics, determined by their reaction with sulphuric acid. Here we can speak of a definite extract with 100 per cent. of aromatics and a raffinate free of aromatics, which two products form the two corners of the famous triangle. Even if the raffinate can be separated and extracted by distillation in a large number of fractions, all these fractions behave similarly *versus* the burning qualities of the kerosine. Further, the boiling range of raffinate and extract are practically similar, which indicates that there has not been any extensive differentiation in the behaviour of the various fractions *versus* the used solvent.

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When we now consider the lubricating-oil extraction we see immediately the great difference in the two processes. There is not a satisfactory chemical method for the control of the separation. The refractive index method, based on the aromaticity of raffinate and extract, is not very illustrative of the quality of the raffinate, and can be used only for control of the process once the principles for a certain feedstock have been definitely established. The other methods in use, such as viscosity index and viscosity–gravity constant, are physical characteristics which have been shown to have a certain relation to the quality of the raffinate. However, here again these characteristics can be used only when we realize that they never have an absolute value. It is well known that the viscosity index is not an absolute value indicating whether an oil is satisfactory or not. Oils with high viscosity index (V.I.) are not always better than oils with a low V.I. when they are of different origin. It is not even a *sine qua non* that the higher the V.I. the better the oil. What is said of the V.I. also goes for the viscosity–gravity constant. But as the V.I. is in general use for the characterization of lubricating oils, it will be used further in this discussion.

From the above it will be clear that the study of the solvent extraction of lubricating oils is much more complicated than the study of kerosine extraction, and that the simple triangle representation is not sufficient to fully explain the phenomena encountered.

Before we can understand why one solvent has a different effect on a certain lubricating oil from another, it will be necessary to study the composition of the various lubricating-oil base stocks. It is my opinion that the investigation of the base stocks for solvent refining has mostly not been carried out completely enough to provide all data necessary for a full understanding of the results of the actual refining process.

Lubricating-oil fractions in crude oil are accumulated in the residue (or topped crude) from the normal distillation process. Besides these lubricating-oil fractions, the residues mostly contain other components, such as waxes and asphalt.

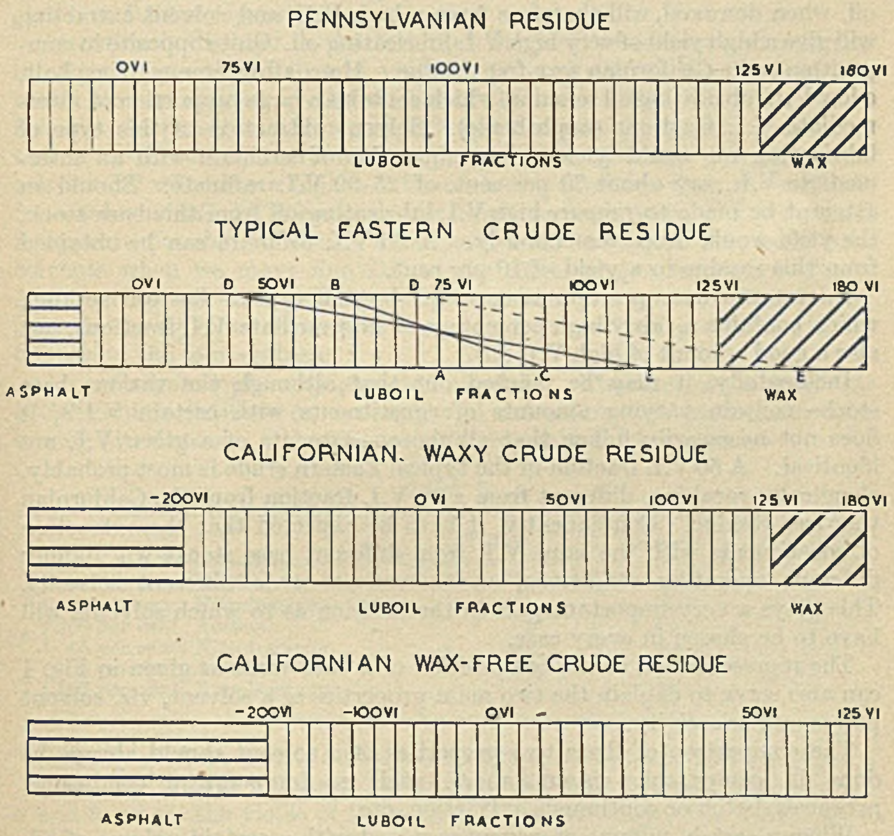
The separation of lubricating-oil fractions from asphalt is mainly performed by vacuum distillation, but it has been found that not all lubricating-oil fractions can be distilled off in high vacuum, as they decompose even below their reduced boiling point. Therefore the heaviest fractions can only be separated from asphalt by other processes, such as precipitation of the asphalt with propane. We may state here already that all single-solvent extraction processes fail to perform a sharp separation between raffinate and asphalt, and are applicable only on distillate lubricating oils. The combination of an asphalt-precipitating process and a solvent-extraction process will be discussed later.

Vacuum distillation does not produce a separation between lubricating-oil fractions and wax, as their boiling points are in the same range. The only way to perform a separation is by means of a dewaxing, with or without the application of a solvent.

The lubricating-oil fractions themselves consist of a large number of constituents, ranging from paraffinic hydrocarbons, via naphthenic, to aromatic hydrocarbons, with their combinations, and, in addition, each group consists of a large number of components with various boiling points. In view of the application of the V.I. as the yardstick for the solvent-refining processes, we can classify the above groups according to their respective V.I.'s as follows :—

Paraffins high to very high V.I.
Naphthenes low to intermediate V.I.
Aromatics very low to low V.I.

The hydrocarbons containing two basic groups may show high or low V.I. As an example, di-cetylnaphthalene may be mentioned, which, notwithstanding its aromatic character, has a V.I. of 150.


PENNSYLVANIAN RESIDUE

TYPICAL EASTERN CRUDE RESIDUE

CALIFORNIAN WAXY CRUDE RESIDUE

CALIFORNIAN WAX-FREE CRUDE RESIDUE

Fig. 1.

APPROXIMATE COMPOSITION OF VARIOUS CRUDE RESIDUES.

To visualize the main composition of various crude residues reference should be made to Fig. 1, which shows the composition of four representative residues of crude oils.

Along the abscissæ are plotted all the fractions of the residue, say forty fractions of 2·5 per cent., according to their V.I., starting with very low V.I. fractions at the left (the asphalts), and continuously increasing the V.I. until the highest V.I. fractions (the wax) are plotted at the right-hand side. These fractions are assumed to be obtained by successive solvent extraction from the residue, extracting first the lowest V.I. fractions, and gradually increasing the extraction.

The ordinate indicates 100 per cent. of each fraction, and will be used to indicate later which percentage of a certain fraction will stay in the extract and which in the raffinate.

From this figure it can immediately be seen that the lubricating-oil content of the various residues is not the same, as is also the case with the distribution of the various lubricating-oil fractions according to V.I. The Pennsylvanian residue is asphalt free (or practically), and contains a relatively small percentage of low V.I. components. This total lubricating oil, when dewaxed, will therefore have a high V.I., and solvent extraction will give a high yield of very high V.I. lubricating oil. Quite opposite in composition is the Californian wax-free residue. Here, after removal of asphalt, a low V.I. lubricating oil remains, which contains a large proportion of intermediate V.I. fractions (naphthenic). Solvent extraction of this type of lubricating oil would yield a large quantity of raffinate with an intermediate V.I., say about 70 per cent. of 25–30 V.I. raffinate. Should an attempt be made to prepare high V.I. lubricating oil from this base stock, the yield would drop tremendously. A 90 V.I. raffinate can be obtained from this residue in a yield of 10 per cent.

An intermediate position is occupied by the typical Eastern residue, which contains a fairly high percentage of intermediate V.I. fractions, but also a good amount of high V.I. oils.

Incidentally, it may be pointed out that although the various base stocks contain varying amounts of constituents with certain V.I.'s, it does not necessarily follow that all the constituents of a given V.I. are identical. A 50 V.I. fraction in the typical Eastern crude is most probably, chemically speaking, different from a 50 V.I. fraction from the Californian wax-free residue. Consequently, it is to be expected that the extraction of constituents with the same V.I. from different base stocks will require different operating conditions, and sometimes even different solvents. This plays a very important part in the decision as to which solvents will have to be chosen in every case.

The representation of the composition of a base stock as given in Fig. 1 can also serve to explain the two main properties of a solvent, viz. solvent power and selectivity.

The comparison of these two properties of a solvent should always be done in comparable circumstances, such as temperature conditions, pressures, batch or continuous extraction, etc.

When a certain volume of solvent is mixed with a certain volume of oil, the fractions with low V.I. mix with the solvent, whereas the fractions with high V.I. form the raffinate phase. In the ideal case there should be a separation between two fractions, the one with the lower V.I. remaining in the solvent, the other with the higher V.I. in the raffinate. The point where this separation (point *A*, Fig. 1) is located depends on the " solvent power " of the solvent. The higher this solvent power, the more point *A* moves to the right, or the less solvent is needed to keep point *A* in its place.

It is, of course, well known that such an exact separation between two constituents never occurs, and that there will be a distribution of the various adjoining constituents over the solvent and the raffinate phase, which distribution is governed by the extraction coefficient of each constituent in the solvent.

Therefore, the separation is not represented by a vertical line in point *A*, but by a sloping line, *e.g.*, that represented by *BC*, cutting line *A* at the 50 per cent. point. The steeper the line *BC*, the sharper has been the separation between the constituents in the extract and those in the raffinate. This sharpness of separation depends on the " selectivity " of the solvent under the given conditions. Line *BC* therefore represents the separation obtained with a solvent with higher selectivity than a solvent which would give line *DE* for separation.

Attention is directed to the fact that the yield of extract and raffinate in all cases mentioned (line *A* vertical, *BC* and *DE*) is the same, as the yields are represented by the surface of the areas to the left and right of the line of separation. However, it is obvious that the quality of extracts and that of raffinate are not the same. The raffinate obtained from solvent *BC* will have a higher V.I. and better qualities than the raffinate from solvent *DE*, as it contains less fractions with lower V.I. Further, it appears possible to obtain a raffinate with the same V.I. from both solvents when we move line *DE* to the right, deeper into the raffinate area, but the yield of raffinate will immediately decrease. This can be done by using more solvent, or increasing the solvent power of *DE* by increasing the temperature.

An actual example may give definite data. The base stock used was a Californian distillate (non-waxy), and extraction was carried out with aniline nitrobenzene. Results are given in the following table :—

TABLE I.

		Temp., ° F.	Yield raff.	V.I. raff.
a	100 per cent. Aniline . . .	75	88	35
	50 per cent. Nitrobenzene . .	35	78	35
b	200 per cent. Aniline . . .	75	85	39
	45 per cent. Nitrobenzene . .	35	85	33
c	100 per cent. Aniline . . .	75	88	35
	100 per cent. Nitrobenzene . .	35	66	47

A study of these results allows the following conclusions to be drawn :—

The selectivity of aniline is higher than that of nitrobenzene from cases *a* and *b*, where the yields of the raffinates with the same V.I. is higher for aniline, or at the same yields, the raffinate from aniline extraction has a higher V.I.

The solvent power of nitrobenzene is higher than that of aniline from case *c*, where the same quantity of solvent applied resulted in a much lower yield of raffinate for nitrobenzene.

Such results may serve as a guide for the selection of the best solvent, *e.g.*, when a raffinate with intermediate V.I. is required aniline would be chosen. But if we want to make the highest V.I. practically possible, say 60 V.I., nitrobenzene would be chosen because the application of aniline would require enormous quantities of solvent (low solvent power), which would prohibit its use.

From the solvents which are in practical application :—

Sulphur dioxide,
Phenol,
Furfural,
Chlorex,
Nitrobenzene,
Sulphur dioxide-benzene,

we can say that sulphur dioxide has the highest selectivity but a very low solvent power; whereas phenol and furfural have the lowest selectivity but a high solvent power. From this the conclusion may be drawn that for the extraction of Pennsylvanian or Eastern (midcontinent) lubricating-oil fractions, sulphur dioxide is in a very unfavourable position, as the solvent power for intermediate V.I. fractions is very low. The Shell Group have tried to improve the working effect of sulphur dioxide by adding benzene to it, thus increasing the solvent power but decreasing the selectivity, and bringing it in line with the other solvents. However, for the production of intermediate V.I. oils from naphthenic base stocks sulphur dioxide is the most suitable solvent.

As a matter of interest the following table gives a summary of an investigation on the extraction of Colon distillate with various solvents. The quality of the raffinate is characterized by the acid value and saponification number after oxidation with oxygen (312 hours at 120° C.).

TABLE II.

Solvent.	Yield raff.	Specific gravity.	n_D 20.	V.I.	Acid Value, 312 hrs.	Sap. Value, 312 hrs.
Phenol	70	0·883	1·4904	91	0·63	1·3
SO_2	70	0·880	1·4866	96	0·12	0·3
SO_2-benzene	70	0·880	1·4881	89	0·45	0·8
Cresol	70	0·884	1·4916	88	0·65	1·8
Chlorex	70	0·884	1·4896	90	0·60	1·4
Furfural	70	0·883	1·4900	88	0·40	1·0
Phenol	60	0·874	1·4856	96	0·38	0·9
SO_2	60	0·877	1·4841	98	0·10	0·2
SO_2-benzene	60	0·875	1·4862	92	0·12	0·3
Cresol	60	0·872	1·4848	96	0·12	0·4
Chlorex	60	0·876	1·4849	91	0·29	0·7
Furfural	60	0·875	1·4857	95	0·14	0·4
Phenol	50	0·867	1·4803	99	0·30	0·9
SO_2	50	—	—	—	—	—
SO_2-benzene	50	0·872	1·4853	94	0·10	0·3
Cresol	50	0·867	1·4814	99	0·10	0·3
Chlorex	50	0·870	1·4810	96	0·10	0·3
Furfural	50	0·870	1·4832	98	0·17	0·2

Here again the superiority of sulphur dioxide is coming to light, giving a good raffinate with a yield of 70 per cent., whereas the other solvents give yields between 50 and 60 per cent. for the same quality raffinate.

It is interesting to note that the specific gravity and refractive index are not the same for all the raffinates with the same quality. For sulphur dioxide a raffinate with 0·880 specific gravity has the same oxidation stability as a furfural raffinate with a specific gravity of about 0·873. This matter will be returned to later.

It is rather difficult to give actual figures for a representation as shown in Fig. 1. But the Shell Group, in their research laboratories, have succeeded in separating a lubricating-oil base stock in ten fractions, which in this case were characterized by the refractive index. This base stock was then solvent extracted, and afterwards extract and raffinate again separated in ten fractions with the same refractive index as the ten fractions from the original base stock. Data were collected on Hendrick's base stock (naphthenic), and are given in the following table :—

Table III.

Fraction no.	Vol. %.	Ref. index n_D 20.	% each fraction in raff.	% each fraction in extract.
1 . . .	10·0	1·589	9·7	90·3
2 . . .	7·0	1·583	13·3	86·7
3 . . .	5·0	1·580	15·6	84·4
4 . . .	5·0	1·566	27·2	72·8
5 . . .	6·5	1·541	50·0	50·0
6 . . .	12·5	1·505	76·1	23·9
7 . . .	14·0	1·492	83·1	16·9
8 . . .	17·0	1·482	88·3	11·7
9 . . .	19·0	1·472	92·9	7·1
10 . . .	4·0	1·464	96·5	3·5
Raff. yield . .	—	—	65·0	—
Extr. yield . .	—	—	—	35·0

The data from the above table have been plotted graphically and are given in Fig. 2.

The top picture gives the relationship between the volume per cent. of each fraction on the crude oil and the refractive index, whereas the bottom picture shows the distribution of each fraction between extract (left side) and raffinate (right side). As could have been expected, the line of separation is not straight, but is a curve tapering to the ends. It is interesting to note that even the extreme fractions (very high or very low refractive index) are present in both phases, even if it is not in large amounts. For completeness sake it is mentioned that this particular extraction was carried out in seven stages, so a relatively sharp separation may already have been expected.

As a matter of interest, the distribution of the fractions was also determined when the extraction with furfural was carried out in four stages with three stages of backwash, at the same yield of raffinate (65 per cent.). The V.I. of the raffinate in the first case (without backwash) was 77, in the second case 84·3. The effect of the backwash system is obvious, the distribution line has turned a little clockwise, indicating the sharper separation resulting in a better raffinate. The figures also indicate that it is of advantage to reduce the number of stages of extraction and replace them by the same number of stages backwash.

Besides the solvent power and the selectivity of solvents, a third property —viz. the light-heavy selectivity—plays an important rôle. Until now we have considered the base stock from the point of view of chemical constitution, but there is also a physical differentiation between the constituents—namely, their molecular size—which is represented by their boiling points. Every base stock contains constituents with lower and higher boiling points, which from a chemical point of view belong in the same category of aromatics or paraffins. Some solvents have a pronounced solvency for lighter hydrocarbons *versus* the heavier hydrocarbons, which means that a larger fraction of a light paraffin will be dissolved in

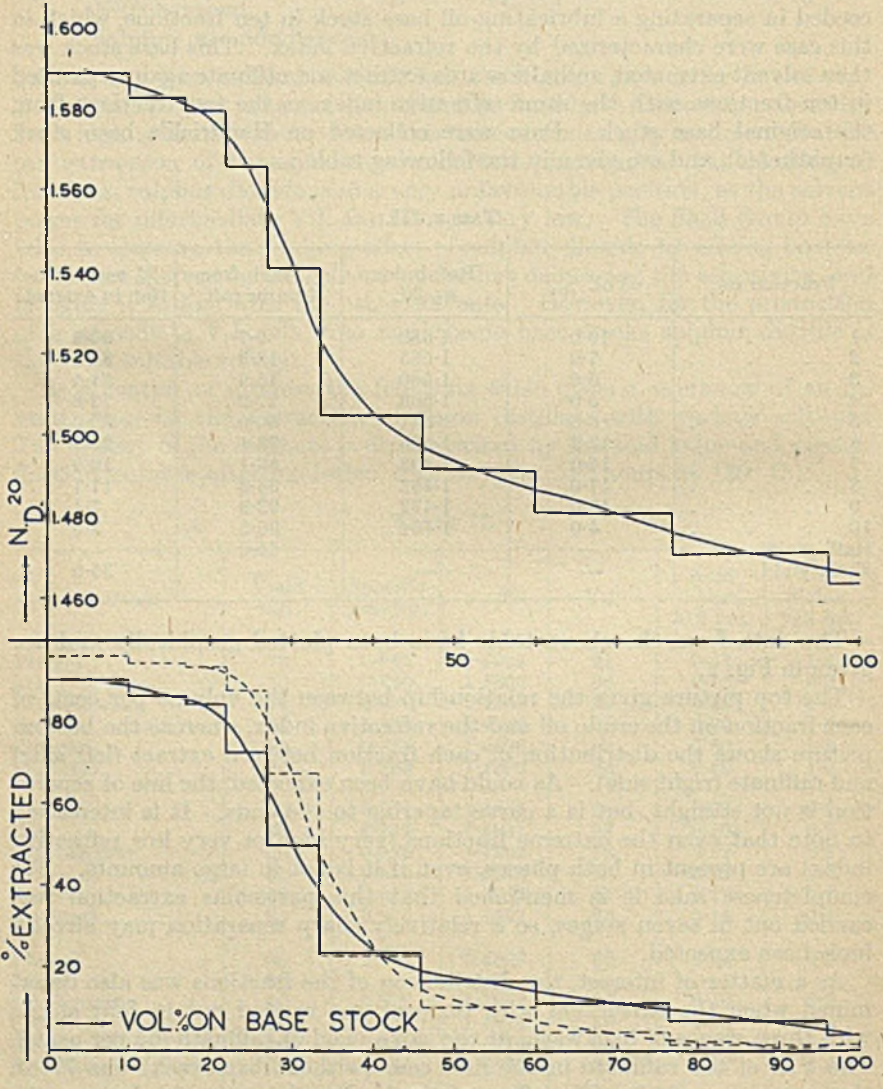


FIG. 2.

FRACTIONAL SEPARATION OF HENDRICKS BASE STOCK WITH FURFURAL.

the extract than of the similar (according to V.I.) heavy paraffin. An attempt has been made to express this property of a solvent in Fig. 3, which expresses the three properties of solvents in one picture.

The front plane of the space figure represents the fractions of the base stock, separated into the various V.I. constituents, similar to Fig. 1. The co-ordinate in depth represents the boiling range of every V.I. group of constituents from high to low boiling points. The separation by a solvent is shown by line *CC'* in the front plane, and if there was no light-heavy selectivity, the total separation would be given by plane *CC'DD'*. However, when light-heavy selectivity plays a rôle, this means that more of the light paraffinic constituents are dissolved in the solvent than of the heavy paraffinic constituents, therefore line *CC'* will move to the left (*EE'*), whereas line *DD'* will move to the right (*FF'*), and the plane *EE'FF'* will represent the total separation. Summarizing, we can say that the extract from a solvent which gives plane *CC'DD'* will contain less lighter high V.I. fractions than the extract produced by a solvent which gives plane *EE'FF'*, which discrepancy is indicated by the content of *GG'FF'DD'*. Fractionation of the second extract should give a light distillate with a higher V.I. than the heavier fractions or the residue. The following actual figures illustrate this :—

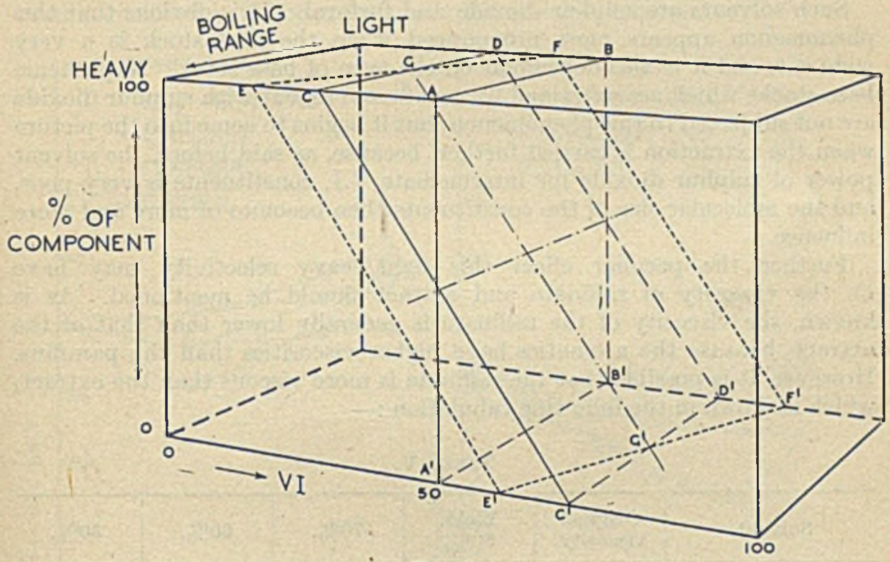


Fig. 3.

STEREOMETRIC VIEW OF SOLVENCY, SELECTIVITY, AND LIGHT/HEAVY SELECTIVITY.

TABLE IV.

	Vol. %.	V.I.
Total extract . . .	100	64
Distillate I . . .	26·0	91
„ II . . .	27·4	60
„ III . . .	26·0	47
Bottoms	20·0	40

Actually, therefore, the fraction I should have been in the raffinate instead of in the extract. It can be said that the light fractions have been over-extracted, the heavy fractions not sufficiently extracted.

The remedy for such a case is obvious—viz., the cuts should have been made before the extraction and extracted separately, by which procedure the extraction can be adjusted to such an extent for each cut that similar quality products would have been obtained for each cut. This method is called the split-feed extraction, and is always advisable if the solvent used possesses a high light-heavy selectivity, and the base stock a wide variety of fractions from light to heavy.

Such solvents are sulphur dioxide and furfural. It is obvious that this phenomenon appears most pronounced when the feed stock is a very wide cut, and it is also dependent on the type of base stock. Naphthenic base stocks which are extracted to a moderate extent with sulphur dioxide are not subjected to this phenomenon, but it begins to come into the picture when the extraction is carried further, because, as said before, the solvent power of sulphur dioxide for intermediate V.I. constituents is very poor, and the molecular size of the constituents then becomes of more and more influence.

Further, the peculiar effect this light/heavy selectivity may have on the viscosity of raffinate and extract should be mentioned. As is known, the viscosity of the raffinate is generally lower than that of the extract, because the aromatics have higher viscosities than the paraffins. However, it is possible that the raffinate is more viscous than the extract, which is shown in the following tabulation :—

TABLE V.

Solvent.	Original viscosity.	Yield. 80%.	70%.	60%.	50%.
Oil V.I., 100	161	—	—	—	—
Phenol	—	163	169	174	187
SO_2 benzene	—	163	166	170	170
Chlorex	—	154	160	168	175
Cresol	—	142	150	162	173
Furfural	—	154	155	156	183
Oil V.I., 80	150	—	—	—	—
Phenol	—	122	112	107	110
SO_2 benzene	—	130	133	140	150
Cresol	—	125	114	110	125
Furfural	—	133	128	127	127

Here it is shown that by further extraction of the oil with a V.I. of 100, the viscosity of the raffinate increases. This is due to the fact that, as there are practically no more aromatics to remove, the solvent is dissolving the paraffinic fractions, and mostly the lightest, first resulting in an increase in the viscosity.

For the extraction of the 80 V.I. base stock the viscosity decreases first, and after all the aromatics are removed the paraffins begin to dissolve. When the solvent has a pronounced light/heavy selectivity a considerable amount of the light paraffinic fractions are already removed during the extraction of the aromatics, and therefore the overall slope of the line will be flat, without a deep minimum, such as is shown by furfural (Fig. 4).

A solvent with a small light/heavy selectivity has not yet removed the lighter paraffinic constituents with the aromatics, and therefore the viscosity of the raffinate drops deeper and then increases again, because a difference in solubility of light and heavy fractions always exists, and this effect then fully comes to light by an increase of the viscosity.

Before it was stated that the raffinate obtained with SO_2 had the highest specific gravity and refractive index (see Table II). This also is caused by the high light/heavy selectivity, because the lighter constituents were readily removed with the aromatics in the first extractions.

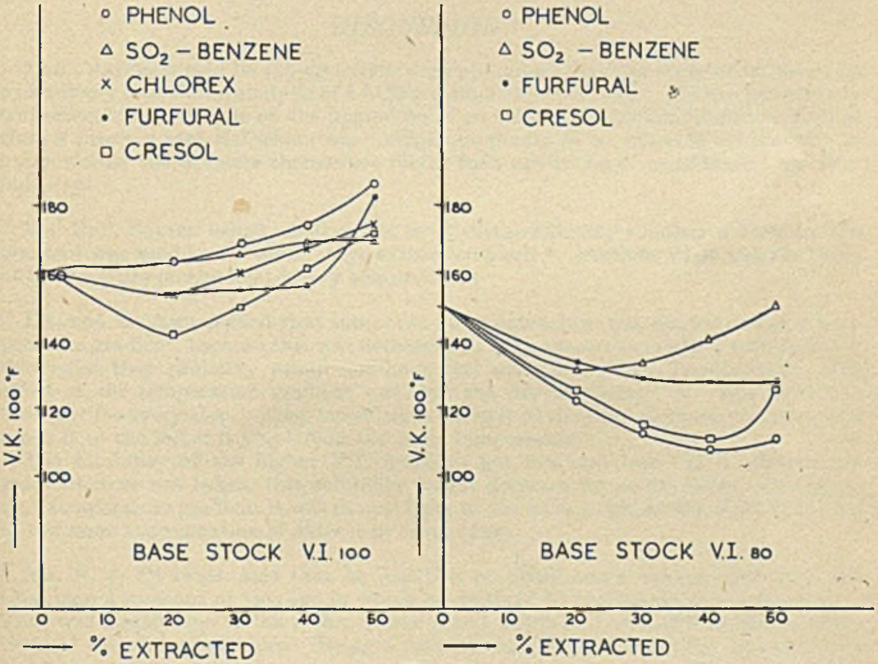


Fig. 4.

KINEMATIC VISCOSITY (CENTISTOKES) AT 100° F.

This characteristic property of all solvents is the reason for the impossibility of extracting S.R. residues immediately with a single solvent to a suitable raffinate. The residues represent the ultimate case of a very wide cut, as the heaviest components, such as asphalt and resins, are present. A single-solvent does not have such a low light/heavy selectivity that all asphalt is removed from the raffinate into the extract layer. Therefore single-solvent extraction processes are applicable only to distillate fractions. The only process capable of processing a S.R. residue is the Duo-Sol process, using a mixture of phenol-cresols as the aromatic solvent and propane as the paraffinic solvent. These two solvents are only slightly miscible, and produce two layers. The solubility of asphaltenes in propane is practically negligible, and therefore all the asphaltenes are precipitated from the raffinate layer into the extract layer. The conclusion may be drawn that it would also be possible to remove the asphaltenes from a S.R. residue by propane precipitation and then solvent extracting the remaining asphalt-free lubricating oil with a single solvent. This was carefully investigated, but it appeared that besides the asphaltenes other very heavy components were present (resins) which could not be extracted. These resins were not precipitated sufficiently by propane alone, but the combination propane-phenol removed all the heavy components into the extract (phenol layer).

From this it is obvious that the Duo-Sol process maintains an exceptional position in the solvent-extraction field, and it is very doubtful whether a single solvent will be found which would produce the same results.

THE INSTITUTE OF PETROLEUM

A MEETING of the Institute of Petroleum was held at the Royal Society of Arts, W.C. 2, on Thursday, 24th June, 1943. DR. DUNSTAN occupied the Chair.

The following paper was read :—

"The Solvent Extraction of Lubricating Oils," by Dr. H. ter Meulen. (See pages 237–248.)

DISCUSSION.

THE CHAIRMAN said he thought they were all agreed that the author had given an exceedingly interesting analysis of a highly complicated problem. He was particularly concerned in his remarks on the upgrading of an apparently useless substance derived from a primary material which was thought originally to be valuable *sui generis*; in other words, the extracts themselves might turn out to be of considerable value in industry.

MR. E. S. SQUIRE asked whether Dr. ter Meulen could say whether a temperature gradient was used in the seven-stage extraction plant? Further, what was the effect of temperature on the light/heavy selectivity?

DR. TER MEULEN replied that this seven-stage extraction was carried out at a temperature gradient, because this was necessary to get a decent separation with furfural. Otherwise they probably would not have had even this sharp fractionation. The effect of the temperature gradient was that the starting-point "A" was moved to the right for every step. They intended to move it to the right, because nature would move it to the left if it was left at the same temperature.

The solubility of the higher V.I. fractions got less and less. If a temperature gradient were not taken, this solubility would decrease for every stage. Operating on a temperature gradient it was moved back to the same point, to the right, resulting in the same concentration of extract in every stage.

MR. E. J. DUNSTAN said that he had had an auctioneer's conversation with the Chairman a moment or two ago in which he declined to participate in the discussion. That was largely due to the rather severe shock which he had had from the implications of the author's lecture. Being a refinery man, he could see the complications in his life increasing very rapidly.

First of all, he thought the author should be heartily congratulated on some work which was of really primary importance in lubricating-oil refining. There had already been recognition of the fact that a very sharp separation was not obtained, but the encouragement to continue with that separation had not really been forthcoming, due to lack of basic information. This paper certainly contained quite a considerable amount of the information required.

He thought that the first stage was recognition of the fact that lubricating-oil distillates should be handled separately—he thought that was implied in the paper—in order to achieve by methods not already available that light/heavy selectivity. Yet he felt from an examination of the literature which had been written on the subject that there was still a great tendency to solvent extract long cuts That might have been altered and he might not be up to date on it, but certainly in the earlier days the tendency had been to extract long cuts and subsequently to fractionate after the contact treatment.

The first stage appeared to be selective distillation—very careful distillation—and the application of the solvent afterwards. The next stage to that was the introduction of numerous stages in the solvent-extraction system. He thought that there they were getting into a mechanical problem—one which would have to be solved by some means or other.

Working an SO_2 process, he looked upon that problem as a very serious one. SO_2 was a solvent that presented the difficulty of maintaining under prolonged conditions gas-tight equipment, and numerous stages, involving a large increase in equipment which had to be mechanically maintained. Nevertheless, it was the mechanical end which appeared to him to be the one to tackle next if this very desirable picture was to be realized to any degree at all.

Dr. ter Meulen said that he was sorry if in going through this pre-print he had omitted a statement about this correction of the light/heavy selectivity. Of course, the solving of this had to be done by separating the feed-stock in the various fractions. The remedy for such a case was obvious. The cut should have been made before the extract and extracted separately, by which procedure the extraction could be adjusted to such an extent for each cut that similar quality products would have been obtained for each cut. That was, as had been said, what should have been done, and in quite a good many plants it was already done.

Mr. Dunstan had touched on a point of the mechanical adventure, as he might call it, into which they were going when they made further separations, because every product would require a solvent recovery. The trouble which was visualized would complicate the plant enormously—he agreed with that. However, there was a Union Oil plant in California which was working on that principle and making three products already. They had gone into that very carefully. The first plant was working SO_2, and the other with SO_2-benzene. In the first they extracted so far that they got a raffinate with only about 50–60 V.I. In the second plant (because the solvent power of SO_2 was too low to obtain a good raffinate with reasonable quantities of solvent) they extracted with SO_2-benezene and made a raffinate with about 90 V.I. The extract which was obtained in that plant was one of those intermediate cuts. Incidentally, in that case it was second-grade lubricating oil, so it was not actually a waste product.

Although they were going in for more complicated plants (with higher maintenance costs and all the other things, on which he agreed with Mr. Dunstan completely), they would give, in his opinion, very high returns, which was of course the purpose for which they were working. It had all only to do with whether it paid or not. He thought that when these intermediate fractions were developed they would find that the value of the fractions would not be considered to be of an intermediate, but in certain cases of even higher value.

Mr. E. J. Dunstan thanked Dr. ter Meulen, but added that he had only served to emphasize his fears.

The Chairman said that one point struck him in passing. Perhaps the author could help them. How were these solvents selected? What had been the basic reason, for example, in selecting chlorex?

As a chemist, one imagined that a selective solvent entered into some sort of loose chemical combination. When the aromatics were dissolved out by SO_2, for example, there was something in the nature of a union between those two. He wondered whether the author could give some idea of what he called the basic principles. Was it just sheer empericism; or was chlorex developed by scientific reasoning?

Dr. ter Meulen replied that there had been a lot of speculation on that, much of which afterwards proved to be not complete hits, but also not complete misses.

The Amsterdam laboratory of the Bataafsche Petroleum My. had done a tremendous amount of work in selecting various solvents based on certain reasoning. They found, working on the polarity of a solvent, that they could reasonably predict whether or not that solvent would be suitable. There were, of course, many misses in that too; there were still cases which did not follow the rule.

Certain polar solvents showed better solvency for—he did not want to use the term aromatic fractions—low-viscosity index fractions then other non-polar solvents. *iso*Propyl alcohol, for example, did not show much polarity one way or the other. They had done some work on that, and had found that *iso*propyl alcohol was completely unsuitable. All these things could be separated into certain polarity groups which might indicate whether they were suitable or not. He agreed with Dr. Dunstan that a definite basis why a certain compound acted as a solvent and why another did not was not definitely stated. He did not think that that had been definitely fixed for all matters of solvents.

Mr. Jarman said he did not know whether it was within the scope of the discussion, but, in view of the remarks which had been made about the extracts, he wondered whether the author was able to give any indication of what should be considered desirable properties of the extracts as distinct from the raffinates in these separations.

Dr. ter Meulen replied that Mr. Jarman was touching on a point which did not exactly come within the scope of the paper. He only wanted to deal with the surface of this whole field, whereas Mr. Jarman would like to pin him down to certain statements about what was actually wanted.

He could give one example which might explain the whole thing. If an extract from a certain Californian oil were taken and distilled in very high-boiling fractions, from an artistic point of view, very nice products were obtained. They were highly coloured, highly fluorescent, and they were absolutely solid, but if a block were made of them, the next day it would be found that it had spread out. If the material were hit with a hammer it just split into a thousand pieces. If it were desired to obtain that product from other products there would be complete failure, because it was not in it. That was only one example. The purpose for which the extract was wanted, and the extract available would not always fit together.

It was only possible for him now to point out what scope there was in that field. Everybody who was interested in it had a field which was so wide that he might find something which suited his special purpose; or maybe he would not find it—he did not know.

The Chairman suggested that in other words it depended on the crude one was working with.

Dr. ter Meulen said that was so, and that even with the same V.I. the fractions were not the same.

The Chairman said that one of these days they would hope to have a very full discussion on the utilization of these remarkable materials.

Mr. Paysant said that, being interested in running a solvent plant, he could sympathize with some of the points that had been made. He had asked himself at times —as this meeting might ask itself—Why did they extract? Why was this process necessary? He thought the answer was that no other process commonly used could do the same work. They could distil oils and do one kind of classification; they could extract them and do another kind of classification.

If they were just out for two products, they had a number of choices amongst the processes, but it looked as though the tendency would be to make a number of products —not just the two end ones, but a number of the intermediates. It had been done; he thought mention had been made of breaking up the oil into narrow fractions by distillation first and then extracting. He believed that the opposite had been done as well, but these procedures were laborious, and he wondered whether the present problems did not alter the choice which Dr. ter Meulen had made in choosing the two-solvent processes rather than the single solvent.

He would like to know more about another point, since it did not seem quite obvious that light/heavy selectivity was altogether a disadvantage. It seemed to him that it might be put to some advantage if at later stages they wanted to cut into oils at very specific points, as they did now with distillation.

Perhaps he could illustrate that in another way. Extraction was used because the job could not be done by distillation; yet in examining an extract Dr. ter Meulen had distilled it, and he had distilled it to examine that light/heavy selectivity. It seemed to him that that was a weapon which might be useful for making these special products at a later stage. In other words, a solvent with marked light/heavy selectivity might be preferable to this two-solvent process, which in effect corresponded to a uniform selectivity.

Dr. ter Meulen replied that the point raised was indeed an interesting one, because it might give the separation of very small quantities of part of the intermediates wanted. He used the data from the table to show that the extract contained high V.I. fractions, but it should not be forgotten that these fractions which were taken out formed not the full group of products in the depth of the space configuration, but only part of that slice it was desired to cut out. What they were aiming to do was to cut out one, two, or three slices from this space configuration. If that were done with a light/heavy selective solvent and it was afterwards distilled, only the back part was cut out from that slice—assuming that the light was at the back—and not the front part, because the front part was not in the extract, it was in the raffinate. Only the back part was in the extract and could be distilled out.

For example, a certain product combination of a paraffin aromatic could be taken, such as ethyl benzene, or any high product like that. There were there hydrocarbons in the same group : ethyl benzene, butyl benzene, propyl benzene. They were in the depth of the picture. Ethyl benzene could be taken at the end and, say, butyl benzene at the beginning. The ethyl benzene was in the extract because it was the lightest, but in the raffinate was the butyl benzene, and the propyl benzene was divided between the two. So only part of that special group was recovered. The results were that the maximum of a special group was not obtained.

Mr. Paysant said that he thought his question was really answered, but he would like to think about it to be convinced. Was it certain that another method would get the whole, in this case, of the propyl benzene in one group ?

Dr. ter Meulen said that it was certain the Duo-Sol process made a steeper cut through the whole thing because it had no light/heavy selectivity. It only depended on how far one extracted with the Duo-Sol plant. It was possible to go straight to the end by adding a lot of solvents and operating at higher temperatures; they could cut deeper into the higher V.I. business, and all the things were in the extract. Then they could theoretically decrease the solvent amount, which would leave another cut in the extract, more to the left, giving a second raffinate which was actually the cut wanted. So anything could be adjusted, decreasing gradually the solvent amount.

The Chairman brought the meeting to a close by saying that it was his very pleasant duty to ask for the heartiest possible vote of thanks to Dr. ter Meulen, who had dealt with a most intricate subject in an extraordinarily clear and lucid fashion.

The vote of thanks was carried with loud applause.

A MODIFICATION OF THE C.F.R. BOUNCING PIN SPRING-TENSION BALANCE AND INSTRUCTIONS FOR USE.

By P. Draper.*

Introduction.

The spring-tension balance designed in the Shell Laboratories and described in the *J. Inst. Petrol.*, Vol. 28, p. 209, had proved so successful, particularly in enabling repeatable octane ratings to be obtained in the range of 90–120 O.N., that the Institute of Petroleum requested the C.F.R. Committee in America to co-operate by designing a less costly apparatus. This has been done very successfully by the Ethyl Gasoline Corporation Yonkers' Laboratory, and the instrument, which is described in this report, has certain advantages over the original model.

Description.

The balance is illustrated in Fig. 1, which is self-explanatory, while further working drawings are given in Figs. 2 and 3.

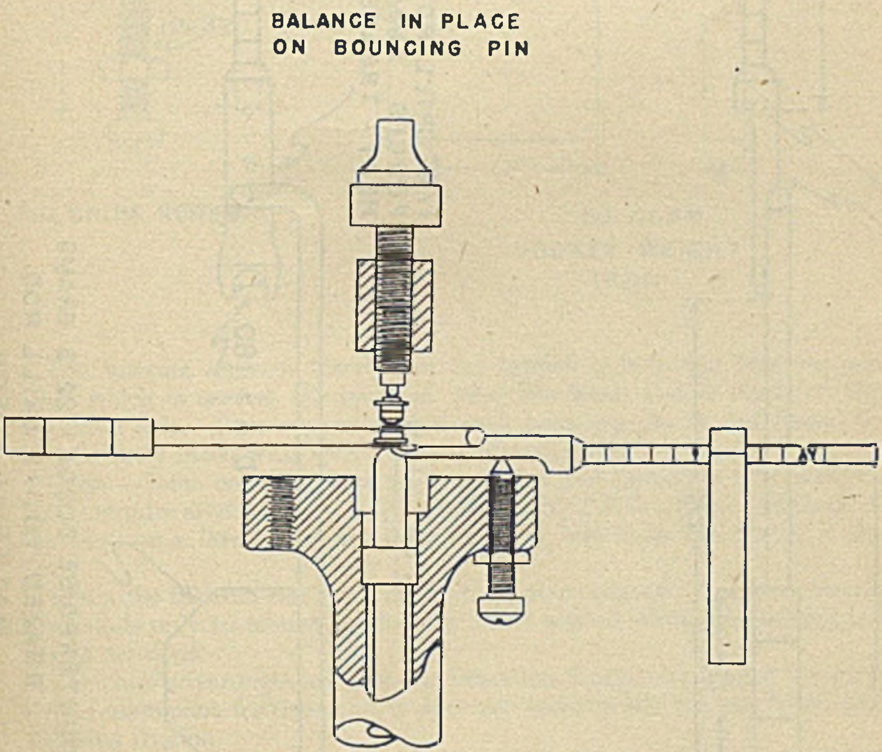


Fig. 1.

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* The Asiatic Petroleum Co., Ltd.

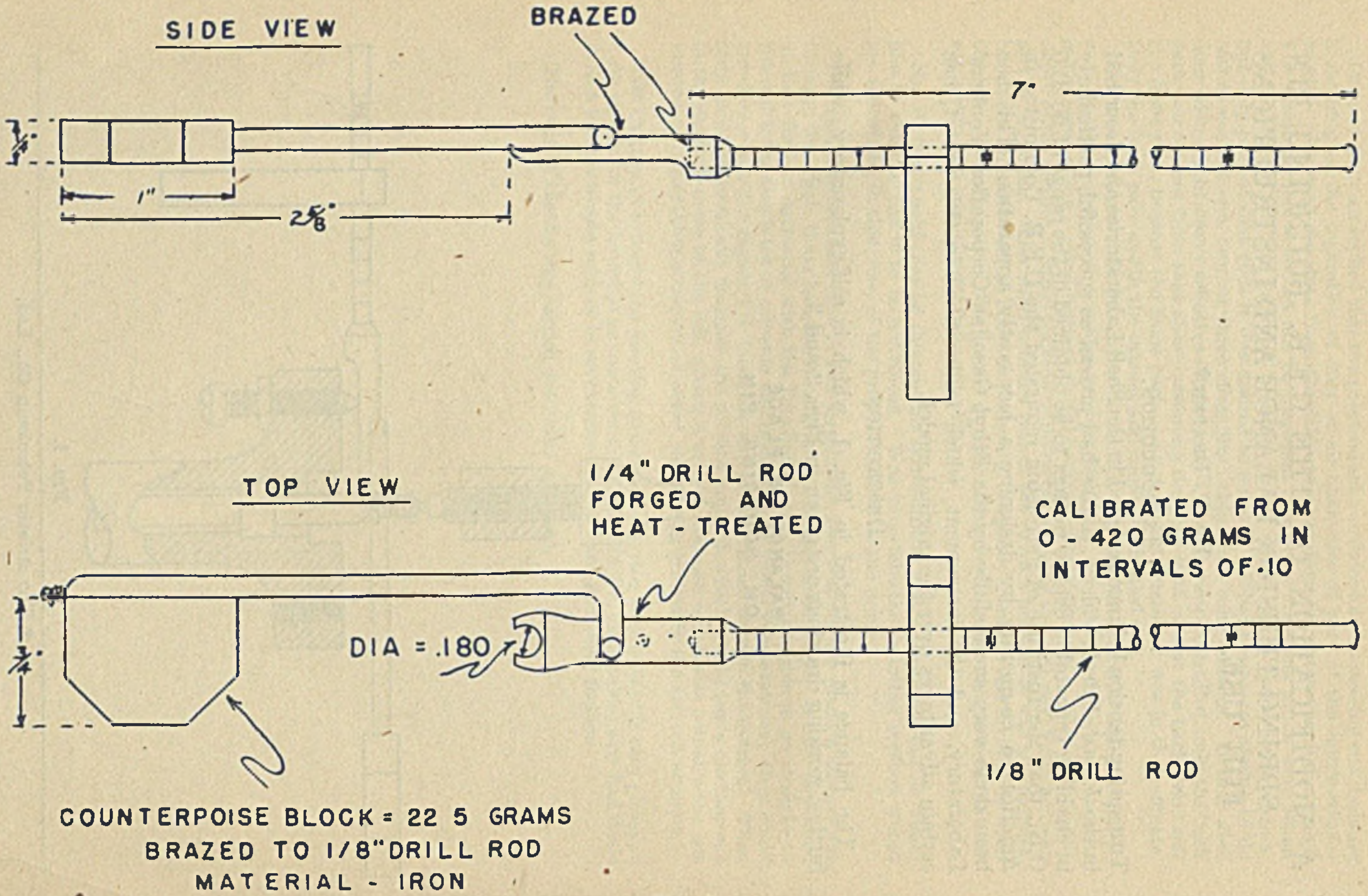
SIDE VIEW
BRAZED
7"
1/4"
1"
2 5/8"
TOP VIEW
1/4" DRILL ROD
FORGED AND
HEAT - TREATED
CALIBRATED FROM
0 - 420 GRAMS IN
INTERVALS OF 10
3/4"
DIA = .180
1/8" DRILL ROD
COUNTERPOISE BLOCK = 22 5 GRAMS
BRAZED TO 1/8" DRILL ROD
MATERIAL - IRON

FIG. 2.

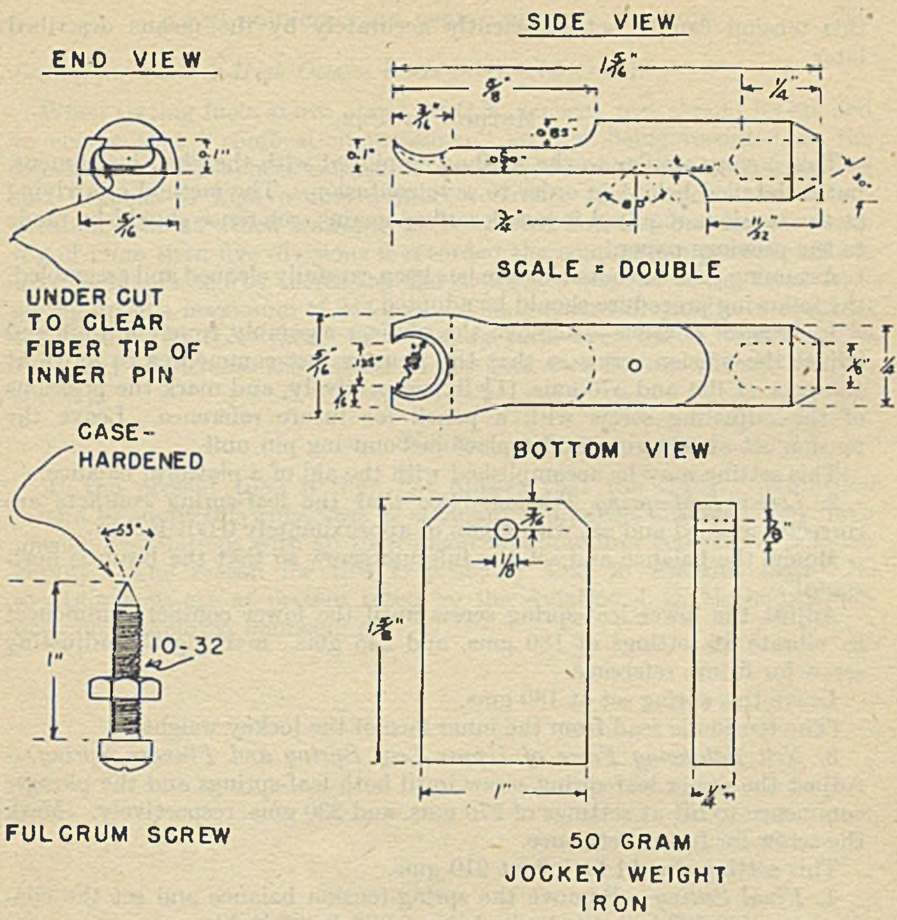

FIG. 3.

The fulcrum screw is inserted in the tapped hole in the bouncing-pin head which is nearest the operator when the lower leaf-spring is on the left-hand side. It is suggested that each bouncing pin in use should be permanently fitted with such a case-hardened screw.

(*Note.*—Some bouncing pins are not drilled and tapped in this position. These require an S.A.E. No. 10 0·19-inch-dia. 32 T.P.I. tapped hole through the head on a line 90° to the bridge piece ¾ inch from the centre of the pin.)

When the fulcrum screw is locked at the correct height it takes a matter of seconds only to mount the balance beam and to commence setting the spring tensions.

The chief advantages are that the beam has 3-point suspension reducing out of alignment friction, and it does not have to lift the pin itself, also reducing friction.

A disadvantage is that the tension of the plunger spring cannot be measured with the balance, but this is not of great importance, as this tension can be set sufficiently accurately by the means described later.

METHOD OF USE.

This is very similar to the method employed with the Shell instrument, but is detailed below, in order to save confusion. The method of arriving at the tensions required is not described again; reference should be made to the previous paper.

Assuming that the bouncing pin has been carefully cleaned and assembled, the following procedure should be adopted.

1. *Plunger Tension.*—Remove the plunger assembly from the unit and adjust the tension screw so that the plunger just commences to move at 455 gms. (1 lb.) and 570 gms. (1¼ lb.) respectively, and mark the positions of the adjusting screw with a pencil for future reference. Leave the tension set at 530 gms. and replace in bouncing pin unit.

This setting may be accomplished with the aid of a platform balance.

2. *Lower Leaf-spring Tension.*—See that the leaf-spring contacts are correctly aligned and set with a gap of approximately 0·001 inch.

Mount the balance and set the fulcrum screw so that the beam is horizontal.

Adjust the lower leaf-spring screw until the lower contact commences to vibrate at settings of 180 gms. and 245 gms., marking the adjusting screw for future reference.

Leave this spring set at 180 gms.

(The tension is read from the inner face of the jockey weight.)

3. *Nett Balancing Force of Upper Leaf Spring and Plunger Spring.*—Adjust the upper leaf-spring screw until both leaf-springs and the plunger commence to lift at settings of 270 gms. and 330 gms. respectively. Mark the screw for future reference.

This setting should be left at 310 gms.

4. *Final Setting.*—Remove the spring-tension balance and set the contact gap to 0·003 inch (its limits being 0·003–0·005 inch).

The bouncing pin is then set for operation, and a minimum of alteration should be made within the limiting marks made on the adjusting screws. No alteration is permissible outside these limits.

Setting for Testing Low Octane Fuels (up to 80 O.N.).

The engine is warmed up and operated at standard knock intensity by running on a fuel of known Octane Number (between 65 and 80) at the appropriate compression ratio or micrometer setting indicated by the A.S.T.M. Guide Tables. A knockmeter reading of 55–60 should then be obtained by *very slight* adjustment of the contact gap within the limits specified above. Should it be necessary to carry out any other adjustment within the marked limits it should be remembered that the nett balancing force of the upper leaf-spring and the plunger determines the sensitivity of the knockmeter, while the tension of the lower leaf-spring should be sufficient to prevent the recording of " combusion pressures " as distinct from knocking.

Setting for Testing High Octane Fuels (above 80 O.N.).

When testing fuels above about 80 O.N. a check test should be applied to ensure that "combustion pressures" are not being recorded on the knockmeter. This check consists of operating the engine on a non-knocking fuel (toluene or high octane number reference fuel blend) at the compression ratio at which testing is to be carried out, if a knockmeter reading of more than five divisions is recorded the combustion pressure effects may be eliminated by increasing the downward tension of the lower leaf-spring up to a maximum of 245 gms. This setting will usually be required for testing 100 O.N. fuels. For testing fuels over 100 O.N. it may be necessary to increase the tension to 300 gms. (see *J. Inst. Petrol.*, Vol. 27, p. 191).

NOTES.

At the present time it does not appear that the C.F.R. Committee intend to adopt this apparatus as standard equipment although they have opened negotiations with an Instrument Manufacturer concerning possible supply. The reason for this is probably that in America high-O.N. aviation fuels are at present rated by the Aviation 1 C. Method, which does not employ a bouncing pin.

ABSTRACTS.

AUTHOR INDEX.

The numbers refer to the Abstract Number.

The original papers referred to in the abstracts marked with an asterisk may be borrowed by Members from the Institute Library.

Geology and Development.

772.* Discovery Rate Continues Below Wartime Needs. L. J. Logan. *Oil Wkly*, 17.5.43, **109** (11), 9.—Excluding semi-wildcats and extensions, 218 wildcats were completed in U.S.A. in April 1943, 27 being productive. While optimistic estimates place the oil so discovered at 150,000,000 brl., conservative estimates give the figure as under 65,000,000 brl., about half the current rate of production. The rate of wildcat completions in 1943 has been only 2900 per year, compared with the P.A.W. goal of 4500.

Ninety-five oil and distillate fields have been found in the first four months of 1943, compared with 105 in the same period of 1942, while there were 18 new pay discoveries in the 1943 period, against 58 in the 1942 period.

In April, Michigan provided two small new fields, Indiana two extensions, Illinois one fair field, one extension and three new pays, Oklahoma four mediocre fields and two extensions. In April, as in March, a comparatively high proportion of the potential new oil discovered was on the Louisiana–Texas Gulf Coast, although East Texas had two discoveries which may develop into major fields. California had two new gas-field discoveries. Ellenburger production, probably of considerable importance, has been found in two tests in Winkler County, West Texas.

Tables show by States and districts the results of wildcatting in April and in the first four months of 1943, with some 1942 figures for comparison; and there is a list of the successful April wildcats giving the name, company and location, depth, producing formation, initial production, type of structure, and method of discovery.

G. D. H.

773.* Brazil's Sharp Production Rise Will Continue When Equipment Available. Anon. *Oil Wkly*, 24.5.43, **109** (12), 49.—Brazil's oil production was 2075 brl. in 1940, 3150 brl. in 1941, and 23,109 brl. in the first nine months of 1942, but on receipt of the necessary equipment it seems likely that the output from known fields will be at the rate of about 225,000 brl./year. The most important production is from the fields of Lobato, Joanes, Candeias, Aratu, and Itaparica in Bahia, near the State capital. The Aratu pool has a gas output estimated at 10,000,000 cu. ft./day. Despite difficulties in obtaining drilling equipment, field work is being continued in the Cruziero do Sul district of Acre in westernmost Brazil. G. D. H.

774.* Canadian Tar-Sands May Yield Oil for War Use. Anon. *Oil Wkly*, 24.5.43, **109** (12), 49.—If favourable results are obtained in the work planned for developing the Athabasca tar-sands this source may provide 10,000 brl. of oil/day.

Much of the sands area is overlain with heavy overburden or lean sands. At present the sands are lightly blasted, excavated by power shovel and transported to the recovery plant by truck. Increased heat conservation seems necessary in the recovery process, for during a test period over 40% of the oil production was used for plant fuel.

G. D. H.

775.* New Zealand Oil Activities Halted. Anon. *Oil Wkly*, 24.5.43, **109** (12), 49.—Four dry holes have been drilled by the Superior Oil Co. in New Zealand to depths ranging 2985–7100 ft. Two wells were in the central part of the North Island, and two on the west coast of the South Island. G. D. H.

776.* Mental Attitude Important Oil-Discovery Factor. Anon. *Oil Wkly*, 31.5.43, **109** (13), 9.—Reflection on the petroleum discovery and producing records of the United

States as compared with those of other countries arouses suspicion that physical conditions in the earth's crust impose fewer and less formidable obstacles to the development of commercial oil-fields over the earth than some mental and social habits. Until the earth at large has been explored to the same extent as the United States, oil will remain undiscovered, no matter how plentiful it may be. U.S.A. constitutes 5% of the total land area of the earth, contains 11% of the total marine rocks of the earth, and only 15% of the earth's total area of important marine rock-filled sedimentary basins of a character favourable to the occurrence of oil-fields ; yet U.S.A. has furnished 54% of the total oil discovered to date. Per unit area U.S.A. has found twenty times as much oil as has been found in the rest of the world, and per unit of favourable area seven times as much as in the rest of the world. There is little evidence to support a conclusion that U.S.A. has seven times as much oil as the rest of the world, but there is abundant evidence that Americans have searched more assiduously for oil and find oil more effectively than any other people. Americans have found much of the oil in countries outside their own.

Oil exploration in U.S.A. is carried on freely and continuously by thousands of independent enterprises which drill year by year 20,000 or 30,000 test-wells at no expense to the Government. Inspired by the financial reward that comes of success, wells are drilled in any unexplored territory, whether the experts think well or badly of its promise.

Over a million wells have been drilled in U.S.A., more than 200,000 being exploratory dry holes. U.S.A. has drilled one exploratory test for each 12 sq. ml. of sediments, whereas in the rest of the world the figure is one for each 1100 sq. ml.

At the current rate of consumption the probable ultimate oil resources of the earth should last for 300 years, although present proved reserves are hardly equal to 20 years' supply.

From time to time the U.S. Government has shown an interest in oil reserves outside U.S.A., and urged exploration in Mexico and South America, as well as securing U.S. participation in Irak.

The American wildcatter would find attractive territory in many European countries, and intensive oil search is required in the Near and Far East and South America, in addition to U.S.A. itself. G. D. H.

777.* Wildcat Promises New Field for Colombia Near Coast. Anon. *Oil Wkly*, 31.5.43, **109** (13), 40.—El Dificil No. 1 promises to open a new field in Colombia. It was drilled to 5930 ft. on a major structure, and is credited with flowing 130 brl./day of 46-gravity oil through a $\frac{3}{16}$-in. choke from a 600-ft. section of porous limestone. A pipe-line to the coast from this area would be short and across relatively easy terrain.

Twenty ml. south-east of El Dificil is another wildcat, Brillante No. 1. G. D. H.

778.* Inspection and Analysis of Formation Samples. L. C. Uren. *Petrol. Engr*, June 1943, **14** (9), 51.—In determining the porosity of a rock sample, the bulk volume of the sample may be determined (*a*) by immerson in a liquid which does not enter the pores, and measurement of the volume of liquid displaced ; (*b*) by saturation with a fluid and then measuring the amount of liquid displaced on immersion ; (*c*) by coating the specimen with a water-impervious substance, with subsequent weighing in air and water ; (*d*) by dressing to some simple geometrical form the dimensions of which are measured ; (*e*) by finding the density of the mineral forming the specimen, and also the pore volume, which, together with the specimen's weight, enable the bulk volume to be found.

The pore volume can be found by finding the bulk volume and the volume of the mineral substance and subtracting. The volume of the mineral substance may be found (1) by gas displacement ; (2) by finding the weight of liquid needed to fill the pores ; (3) by weighing the dry specimen, saturating it with a liquid and then reweighing in the same liquid ; (4) by crushing the specimen to separate the grains which are then placed in a pycnometer for volume measurement.

In order to find the size distribution of the grains in the sample, the grains must be separated. Some rocks crumble readily, while others must be disaggregated by heating and rapid cooling, by freezing liquid in the pores or by dissolving the cement. Before screening, oil must be dissolved from the grains. The size distribution is found by sieving, and by elutriation for the grains passing 200-mesh. The results are generally displayed graphically. G. D. H.

779. Classification of Sedimentary Rocks Related to Kind of Oil Reservoir. W. V. Howard. *Oil Gas J.*, 3.6.43, **42** (4), 70.—From the standpoint of correlation of beds, a classification based on the obvious physical characteristics of sediments may be adequate, provided that it is based on standardized descriptive terms. But if it is required to use the knowledge for the location, development, and production of oilfields, other types of classification are necessary. A genetic classification is needed. The material deposited in any environment depends on conditions within the environment and also on conditions in the area from which material is transported into that environment. Van der Gracht and Krynine have suggested classifications on this basis. The former considers not only the normal sediments of shallow seas bordering coastal plains areas, but also " flysch " deposits laid down in a geosyncline directly previous to the major elevation of the neighbouring land. The basin of deposition may range from shallow to deep, and the environment from marine to continental. The sediments tend to range from fine clastics below to coarse clastics above. Krynine's preliminary classification refers to sandstones, and subdivides these into " clean " (formed after long decay in peneplained areas or by re-working of previously deposited quartzose sediments), " greywackes " (with much slate, shale, chert, and micas and other relatively unstable minerals indicating fairly rapid derivation from an uplifted land mass worn down to the level at which mildly metamorphosed rocks occur), and " arkoses " (felspathic sandstones). As the mountains are worn down further, erosion and deposition are less rapid and chemical action becomes more important, resulting in the formation of such materials as granite wash.

However, the nature of the terrane uplifted has as much to do with the sediments deposited as the amount of uplift.

Normal (quartzose) sediments are derived from relatively flat-lying land masses on which erosion is slow and chemical decay intense. They tend to be uniform in texture and composition over long distances, the sandstones being clean, and as blanket deposits they produce on structure. Wedge-edges are rare. Limestones and dolomites make up much of the section, and may have been uplifted, and eroded over wide areas. The shales are largely clay shales. The clean, uniform sands may be expected to give high primary oil recoveries except with dissolved-gas drive.

The flysch sediments arise from relatively rapid denudation of an uplifted land area, with deposition in a geosyncline. Depending on the relative rates of deposition and sinking of the geosyncline, the beds will be a mixture of marine and continental deposits, often associated with coal. Rapid variation in short distances is common, with numerous wedge-edges, lenses, sand bars, and other forms of stratigraphic trap. The sands tend to be dirty. Limestones are rare, thin, and of little extent. Correlation is difficult. Production on structure is frequent, but stratigraphic traps are commoner than in the normal type sediment. Irregularities of porosity and permeability, with limited extent of the reservoirs, make water- and gas-cap drive less likely.

Molasse sediments will be arkosic if the mountains have been denuded to the granite. They result from rapid erosion of steep slopes, and are deposited mainly in foredeeps. They are poorly sorted and poorly weathered. As the basin fills they tend to get finer, and may go from marine to continental. Limestones are generally absent. Flysch and molasse deposits are not sharply separated. Stratigraphic traps are common in molasse, even of continental origin. Their irregular permeability prevents high recoveries.

Often the later molasse sediments are continental, but at times they remain marine and grade into the normal type. Sometimes they include beds of granite wash (highly weathered arkose), and limestones and dolomites may be interfingered with this. The latter point to dominance of chemical over mechanical erosion. G. D. H.

780.* Colombian Development Prospects Have Improved Materially During Year. Anon. *Oil Wkly*, 7.6.43, **110** (1), 47.—The Shell has drilled ten producing wells in the Casabe field which was discovered last year. Two sands have been proved, and the reserves are estimated at over 135,000,000 brl. Production has been found more recently in the Dificil field of the Departmenta Magdalena. This production, which comes from a porous limestone at 5928 ft., is Colombia's most northerly oil-field.

Two new structures have been found on the Barco concession. G. D. H.

781.* Mexico Reports Discovery of New Producing Horizon. Anon. *Oil Wkly*, 7.6.43, **110** (1), 47.—A new producing horizon is reported in the area around Minatitlan, Vera Cruz. This discovery well is in the north-west corner of the field and is giving 2800 brl./day.

In the Poza Rica field two good wells have been completed recently. One flowed initially at 3000 brl./day from 2385 m., and the other at 3500 brl./day from 2990 m. G. D. H.

782.* To Drill Canadian Wildcat 65 ml. East of Edmonton. Anon. *Oil Wkly*, 7.6.43, **110** (1), 47.—Preparations are being made for drilling midway between Bruce and Holden, Alberta. The area, which is 18 ml. west of the Viking and Kinsella fields, has good surface indications of oil. G. D. H.

783.* To Drill Costly Wildcat in Canadian Waters. Anon. *Oil Wkly*, 7.6.43, **110** (1). 47.—A 12,000-ft. test is to be drilled in Hillsborough Bay adjoining Northumberland Strait. The test is on a large structure mapped at the surface and confirmed by seismograph, and lies under a mile south-west of a well taken to 5965 ft. without finding signs of oil.

Seepages have long been known in this part of Canada, and near Moncton, New Brunswick, is a small field yielding mainly gas. G. D. H.

784. Importance of West Texas Ordovician in National Picture Still Not Clear. H. F. Simons. *Oil Gas J.*, 10.6.43, **42** (5), 30.—Ordovician developments in West Texas show that the formation is important, but there is not yet sufficient information to determine fully the formation's potentialities. Where Ordovician oil has been found beneath Permian fields the trap has been anticlinal. The Permian structure has been a rather broad and gentle anticline, a type which is common. However, some Permian structures are small and steep, and there is considerable Permian production from reef and stratigraphic traps, but in these cases no deep tests have been made. The Ordovician structures have been found to be much sharper than the Permian structures, and therefore the extent of the Ordovician reservoirs is likely to be less than that of the Permian pools. It is possible that there may be Ordovician production below Permian features which lack adequate closure.

The seismograph will probably be used more widely in the future in finding Ordovician structures. The Ellenburger seems to be reasonably uniform, the pools generally having gas-caps and probably an effective water-drive, with a pay thickness of 80–150 ft.

Other Ordovician pays may have possibilities as well as pays below the San Andres and above the Ellenburger, for practically all the Ellenburger wells have shown possible production in the upper formations.

10,000-ft. West Texas wells have cost about $350,000, but the cost will probably be reduced to $150,000 and eventually much less. G. D. H.

785. Oil Zones of the United States : Pennsylvanian. Anon. *Oil Gas J.*, 10.6.43, **42** (5), 64-C.—In the Alleghany Plateau region, Pennsylvanian production is largely limited to the central part of the basin, the most important sands being the Little Dunkard and Big Dunkard of the Conemaugh, the Burning Springs sand of the Alleghany, and the Second Cow Run and Salt sands of the Pottsville. There are interbedded gas-sands. The chief Pennsylvanian production of the Illinois basin is at the southern end of the La Salle anticline (Siggins, Casey, Claypool, Upper Partlow, Bridgeport, Biehl, and Buchanan sands). In the Centralia area, on the Du Quoin anticline, the Petro sand is productive. The principal Pennsylvanian production in Indiana is from the Mansfield sand of Pottsville age. Much of the earlier production is Eastern Kansas, North-east Oklahoma, and the McAlester basin, extending across the Hunton and Chautauqua arches and the buried Nemaha ridge, came from a series of

Pennsylvanian sands, the age of which increases to the south (Stalnaker, Layton, Peru, Prue, Bartlesville, Burgess, Burbank, Hoover, Calvin, Gilcrease, Papoose, Cromwell, Lyons, and Dutcher). On the Central Kansas uplift there is important Kansas City–Lansing lime production. On the Bend Arch also the age of the Pennsylvanian producing horizons increases to the south. In Eastern Wyoming the Minnelusa is productive, and the extensive Tensleep sand in Central and Western Wyoming.

Additional Pennsylvanian production may be found in the basins flanking the Bend Arch, and Minnelusa production may extend down the east side of the Denver basin, some small pools already having been found in Western Kansas. Tensleep production is possible round most of the Rocky Mountain basins. The Salina basin of Eastern Kansas may contain Pennsylvanian oil.

Most of the Pennsylvanian sand production is near uplifts associated with the Appalachian folding, for at its peak in Pennsylvanian times the uplifts of the Appalachians, Ouachitas, Ozarks, Arbuckle, Wichitas, etc., were subjected to strong erosion. The low areas sank, giving a thick series of alternating clays and sands with some limestone. Sometimes the basinal sediments were uplifted, and when limestones were exposed they frequently acquired sufficient porosity to become reservoir rocks. G. D. H.

786.* Well Drilling Decline Continues in May. Anon. *Oil Wkly*, 14.6.43, **110** (2), 57.—The average weekly rate of well completions in May was 339, compared with 355 per week in April. During the first five months of 1943 7263 wells have been completed, against 9204 in the corresponding period of 1942. Relaxation of drilling regulations has caused California to drill 615 wells in the first five months of 1943, whereas only 315 were completed in the first five months of 1942; in Kentucky the corresponding figures were 115 and 57 respectively. Activity in Texas is greater than in any other State, and both completions and rigs in operation are scarcely more than 50% of the 1942 figures.

Completion data are tabulated by States and districts for May and for the first five months of 1943, with some 1942 figures for comparison. G. D. H.

787.* Intensive Development of Oil-fields Has Increased Petroleum Output of Peru. Anon., *Oil Wkly*, 14.6.43, **110** (2), 59.—The downward trend of oil output in Peru has been stopped, but there are no signs of a sharp increase in production. In 1936 17,593,000 brl. of oil were produced, an all-time peak, 11,922,000 brl. in 1941, and 13,500,000 brl. in 1942. Exploration and leasing have been very restricted in the past year, due to tax increases and refusal of applications for concessions.

The Ganzo Azul field of Eastern Peru, opened in 1939, is now producing more oil than is required in the surrounding district, and marketing of oil in Brazil and Uruguay is being planned. The oil is in the Lower Cretaceous on an anticline which is 16 ml. long, 7 ml. wide, and has 3500 ft. of closure.

In North-west Peru, La Brea–Parinas produces from the Eocene at depths of 60–6000 ft. on a faulted, folded structure. The output from 1750 wells spread over 13,500 acres is 25,000 brl./acre. The cumulative production exceeds 225,000,000 brl. The Lobitos field is geologically similar to La Brea–Parinas. It covers 2000 acres, and has an output of 7000 brl./day from depths of 3000–6000 ft. The cumulative production is about 55,000,000 brl. The 50-year-old Zorritos field now produces from a few wells only. The oil is in faulted Miocene sands at depths of 300–1700 ft. The productive area is about 400 acres, but not fully defined.

Peru has one large refinery and two small skimming plants. Oil is Peru's principal industrial fuel; it is also used on the railways, and some is exported.

A table gives the oil production and consumption figures for recent years. G. D. H.

788. Lithification Processes and Early Oil Formation in Sediments. W. V. Howard. *Oil Gas J.*, 17.6.43, **42** (6), 92.—Cementation or lithification depends on two main factors: the composition of the water in which the sediments are deposited, and the rate of deposition. Calcium carbonate, the commonest cement, is carried in solution as the bicarbonate. It is probable that much of the annual increment of calcium and carbonate reaching the sea is precipitated, as the sea is nearly saturated with calcium carbonate. That part of the calcium carbonate secreted by animals as shells and skeletons eventually reaches the sea-floor, where there is continual solution and reprecipitation of this material, with the result that the openings between grains of clastic material become filled or partly filled with calcite. This tends to cement the grains together.

Actually deposition of calcium carbonate takes place almost everywhere in the sea, and limestone is formed where there are no other sediments deposited with it. Hence the greater proportion of limestone in normal than in flysch sediments and their almost complete absence in molasses.

Cementation is not a question of age, but rather of conditions of deposition, and the comparatively recent history of the earth is probably such as to make the study of recent sediments insufficient to show all that should be known about older sediments.

Trask found an average of 1·6% of organic matter in recent sediments, and if five-eighths of this becomes oil this would be 3 gal./14 cu. ft. of sediment, or about 222 brl./acre-ft. Hence a drainage area three or four times the size of an oil-pool would provide *in situ* origin of oil without migration from other beds and without much migration along the reservoir bed.

The Gaspar limestone of Northern Alabama has oolites with calcite core, a ring of bitumen, and then more calcite, pointing to bitumen deposition when the limestone was being formed. The Anacacho limestone of Uvalde County, Texas, is simply a limestone "sand" cemented by asphalt, and treatment with carbon tetrachloride leaves a heap of loose limestone grains. G. D. H.

789. Post-War Demand for U.S. Crude. W. V. Howard. *Oil Gas J.*, 24.6.43, **42** (7), 78.—It is reasonable to assume that the post-war crude demand will continue to increase at the pre-war rate—*i.e.*, by about 60,000,000 brl./year, giving a total of 1,700,000,000 brl. in 1947.

The discovery rate has been falling for nearly five years, and even if last year's discoveries are allotted their probable recovery rather than their estimated proven reserves, they are still 45% below the output.

Based on existing conditions, the trend of discovery, and the present transportation system, it is probable that the 1943 demands can be met, but that 1944 production will be about 40,000,000 brl. below estimated demand. The peak of production from existing fields, together with additions at a rate comparable to that provided by new fields during the past four years, will probably be reached in 1944, followed by a decline to about 1,350,000,000 brl. by 1947. Texas will probably reach its peak in 1945, when its output will have risen by 100,000 brl./day. California, Louisiana, Kansas, and Arkansas are likely to reach their peak this year.

In the past two years about 24,000 wells have been abandoned, and this calls for the drilling of at least 15,000 producers per year, and preferably about 20,000. If these numbers are not attained, then drilling immediately after the war will have to be at an even higher rate, perhaps 30,000–35,000 per year.

While secondary recovery methods increase the production of individual fields, their effect is relatively small when considered on a national basis. A growing shortage, probably accompanied by higher prices, encourages the use of these methods. If sufficient wells cannot be drilled in U.S.A., then additional oil supplies will have to be drawn from South America and Mexico.

When the liquid oil supply fails to meet demands, resort must be made to the extensive oil-shale deposits, the tar-sands of Canada, and the low-grade coals, all of which will yield oil at a price.

A graph shows the production of the major U.S. oil-producing States from 1935 onwards, with extrapolation to 1947. The peak year for each State is shown, and the possible deficiency in 1947 is indicated. G. D. H.

790. Derivation of Reservoir Rocks. Part I. W. V. Howard. *Oil Gas J.*, 24.6.43, **42** (7), 158.—Oil has been found in weathered granite and the Madison limestone of Montana, Wyoming, and Alberta. The sequence of events was probably : (1) formation of rock which later became reservoir ; (2) exposure to erosion ; (3) development of porosity ; (4) burial beneath sea ; (5) entrance of oil-forming material and deposition of sealing formation. This sequence was probably followed in reservoirs responsible for more than half of the world's production of oil.

The cycles of uplift and sedimentation are generally oscillatory, and sediments of the normal type start and conclude each complete cycle, and may be interbedded in sections predominantly of the greywacke or arkose classes. All the processes which lead to the formation of oil reservoirs are involved in the areas which yield sediments of the normal type and in the areas in which they are deposited. These processes are, however, modified in deposits of the flysch and molasse type.

The breakdown of sandstone or conglomerate by removal of the cement and changes in the constituent fragments gives reservoirs of four types: (1) The sea may advance over a partly eroded sandstone or conglomerate before disintegration is complete, thus creating truncated sand reservoirs beneath an unconformity. It will have widespread permeability. (2) Much disintegrated sandstone and conglomerate form sands and gravels in rivers and lakes. Advancing sea may not remove these deposits generally, and the buried river deposits form reservoirs of the shoestring type. (3) Unconsolidated rock mantle may be picked up and redistributed by an advancing sea as numerous sand lenses overlapping shoreward. They tend to lie on old land surfaces, and may have impermeable streaks and constitute near-shore sand bodies and buried sand-bar reservoirs. (4) Blanket-type sands are said by some to be re-worked material deposited by sea advancing over land, the fine material having been largely removed, whereas others maintain that the sand is carried to the sea and deposited. Conglomerates are generally believed to be basal, formed by sea advancing over a pebble- and sand-strewn land mass.

In decomposition the cement and accessory minerals of sandstones are added to the list of products derived from sandstones. G. D. H.

791. Rigs and Drilling Wells Increase in May. Anon. *Oil Gas J.*, 24.6.43, **42** (7), 190.—The 1358 wells completed in U.S.A. in May 1943 were seven more than in April, but forty-seven fewer oil-wells were brought in. 499 wells were dry. For the third consecutive month the number of wells in the 5000–10,000-ft. class showed an increase. So far this year total completions are 4·4% below the 1942 figure, and the number of oil-wells is 14·9% below the 1942 level.

A table gives by States the number of completions, oil- and gas-wells, the footage, number of active rigs, and the number of wells in various depth ranges.

G. D. H.

792. Oil Zones of the United States: Permian. Anon. *Oil Gas J.*, 1.7.43, **42** (8), 48-C.—Permian oil production in U.S.A. is confined to three areas, of which the Permian basin of Texas and New Mexico, and the Amarillo–Hugoton area are the most important. The producing limestones and associated clastics become progressively younger from north to south, limestones, dolomites, and granite wash of Wichita–Albany age being productive in the Panhandle area. In the central part of the basin the San Andres limestone is the principal oil horizon. Still farther south and west, the Whitehorse group yields most of the oil. On the west flank of the Fort Stockton high, the Delaware sand (equivalent to the Lower part of the San Andres) is highly productive. In the last stages of infilling of the marine basin, the producing sands of the Red River district were formed; this is continuous with Permian production in the Anadarko basin.

In Wyoming, especially round the margin of the Big Horn basin, the Embar yields important quantities of black oil.

Most of the Permian deposits in other parts of U.S.A. are continental, thereby precluding oil production, but considerable extensions of known producing belts is possible.

Many of the West Texas fields have only been drilled into the top of the Permian, and the area between West Texas and the Panhandle field has been little prospected. There are possibilities of Permian oil in Southern Oklahoma, both north and south of the Wichita–Arbuckle mountain belt. Western Wyoming may provide Permian oil in several of its basins.

The Permian represents the last marine deposits of the Midcontinent area, so that no production can be expected above it north of the Ouachita–Mexia–Balcones belt, but this does not include the Rocky Mountain area where basins did not form until long after the Permian. G. D. H.

793. Mexican Production Rising. Anon. *Oil Gas J.*, 8.7.43, **42** (9), 17.—The Petroleos Mexicanos oil production fell from 136,843 brl./day in January 1942 to 67,820 brl./day in November, but rose to 88,465 brl./day in April 1943. Poza Rica is the most prolific area under Pemex Management, and current production averages about 57,500 brl./day.

Independent companies normally produce 4000–4580 brl./day. G. D. H.

794. Completions Rise Sharply in California Heavy Fields. L. P.Stockman. *Oil Gas J.*, 8.7.43, **42** (9), 18.—It seems likely that 1500 new wells will be drilled in California during 1943. This figure is above the past yearly average, but the footage will be below the average figure because much of the projected development is in fields with pays at 1000–3000 ft. Portable units are being used extensively in this drilling campaign. The amount of drilling carried out during the first half of 1943 was about twice that for the corresponding period of 1942.

At South Belridge, where production is found at 700–1300 ft., wells are completed in about a week. There is increased drilling activity at Midway-Sunset, Elk Hills, Round Mountain, Newhall Potrero, Brea Olinda, and Huntingdon Beach. Much of the current development consists of drilling undeveloped acreage in the older fields, such as Buena Vista Hills, Coalinga, Midway-Sunset, Mount Poso, Round Mountain, Santa Maria Valley, Huntingdon Beach, Torrance, Elk Hills, Ventura Avenue, Newhall Potrero, East and West Coyote, and Montebello. Wildcatting has not been especially successful. Thirty-five new wells are expected to be drilled at Elk Hills, where much extension work remains to be done. Miocene production was discovered there a year ago, and although the sand is fairly tight, there are indications of a large reserve.

Californian crude-oil production seems to have reached its present peak because of the application of the maximum-efficiency-rate factor, and the necessity of reducing high gas/oil ratio wells in order to eliminate gas waste. G. D. H.

795. Porosity Limit with Depth. H. W. Bell (with discussion by W. V. Howard). *Oil Gas J.*, 8.7.43, **42** (9), 66.—At some depth, the plasticity of the rocks due to temperature and pressure will become such as to eliminate porosity, and so prevent the obtaining of any fluid. The fluid in pores will resist compressional collapse of the pores. If the maximum compressive strength of the rock material is 10,000 lb./in.^{2}, then if the effective collapsing force is 0·692 lb./in.^{2}/ft. the porosity will vanish at about 14,500 ft. Gutenberg's data suggest that the limiting depth will be 21,000 ft. at 60° F., but considerably less at 400° F.

It is possible that some reservoirs have lost their porosity at 14,000 ft., but others may have reasonable porosity at 80,000 ft. During geological time it is possible that failure of a reservoir could take place at a pressure between the elastic limit and the ultimate compressive strength. Before the porosity disappears the oil may go into the gaseous phase and reach a higher density than its liquid, and as the porosity vanishes it may be driven into the pores of surrounding shales, probably ultimately entering into chemical combination with them.

Discussion. When a reservoir rock with its fluids is surrounded by impervious beds, the lack of avenues for fluid escape means that the depth at which the pores collapse will be very great. This is modified by the tendency for silica to be dissolved from small grains and at points highly stressed, with subsequent deposition around the larger grains at less-stressed points.

Cores from sands which have been deeply buried by amounts which can readily be estimated provide rock sections in which the amount of re-deposited silica can be observed. Incipient rupture of quartz grains is shown by strain shadows. If these shadows extend beyond the original grain into the re-deposited silica they indicate that the reservoir has begun to show signs of collapse. Sections can also be cut from sediments, now exposed, which have been buried extremely deeply. G. D. H.

Drilling.

796. Protection of Surface Hole in Lindsborg, Kansas, Wells. N. Williams. *Oil Gas J.*, 29.4.43, **41** (51), 45–47.—Certain problems, unusual in Kansas generally, but met in one field, are described. The principal trouble has been occasioned by porous, aqueous gravel beds, if not cavity sections, in the surface formations that result in loss of returns of drilling fluid. Close to the surface there is a water-saturated loose sand or gravel bed which washes into the hole and causes caving unless protected. Although the condition is not universal over the field, it is sufficiently prevalent to offer a threat to all drilling. Special practices and precautions have had to be adopted in drilling and casing these formations to ensure adequate protection.

These conditions usually call for the running of two strings of surface casing as against one in normal Kansas operations. The first of these is required to protect the shallow fresh-water sands. Field regulations specify that a minimum of 175 ft. of pipe be set and cemented to the top. Operators usually find a good seat for this string at 185–190 ft. Cementing of both strings is discussed.

On one occasion, the operator, unable to cement off the formation by various other methods, resorted to drilling a second hole behind the pipe. First, several hundred sacks of cement were pumped in the usual manner without getting circulation. Then an attempt was made without success to seal the formation by squeezing cement behind the pipe through perforations just above the gravel bed. Attempts to run in cement behind the pipe through a 1-in. pipe in the annular space also failed. It was then decided to try drilling another hole through which additional sealing material could be pumped into the formation. For this the rotary table was skidded a few inches, just enough to permit clearly the 8⅝-in. casing. A 6-in. bit was used, and the hole followed the back side of the pipe down to the top of the formation. First, quantities of cotton-seed hulls and heavy mud were pumped. Next large quantities of burlap were pushed down. Successive batches of burlap and heavy mud were forced into the hole, and by raising and lowering the pipe this was tamped and worked down around the back of the casing above the bed. Finally, after a number of days, a seal was effected and the hole was filled with cement.

The casing programme and other details are given briefly. A. H. N.

797.* Unitized Skid Transports Entire Rig-Lifting Setup. Anon. *Oil Wkly*, 3.5.43, **109** (9), 15–16.—This short note describes a unitized skid which was designed to provide adequate protection against haulage accidents and to effect saving in time and physical effort. A. H. N.

798. Direct-Current Rigs for Deep-Drilling Operations. R. A. J. Dawson. *Oil Gas J.*, 6.5.43, **41** (52), 129. *Paper Presented before American Petroleum Institute.*—Comparative cost and engineering-design studies are made and given in some detail. The general conclusions are : Large electric rigs must definitely be tailor-made of the very best of available equipment, but they fit very well into drilling programmes of certain types. There is no question of the many unique advantages of electric power in the drilling of deep, remote wildcats, and it is hoped that the oil industry will become increasingly cognizant of this economic oversight. An investment of approximately 250,000 dollars is admittedly a large sum, but such steady savings in operation costs are possible on the deep penetrations of to-day that the 50,000 dollars difference between the price of electrical and steam equipment can soon be overcome.

The future of electric drilling depends on the manufacturers' ability to prove the economy and flexibility of electric power, and to do this they must develop technical personnel that is familiar with actual drilling procedure. Development of such personnel will take time, but only by such a procedure will the oil industry capitalize on those flexible designs that are directly related to future economical operation.
A. H. N.

799. Well Logging. M. E. Kelly. *Fuel*, 1943, **22**, 55.—A short review is given of the basic principles of electrical, gamma-ray, and neutron logging. J. W. H.

800. Patents on Drilling. A. L. Parker. U.S.P. 2,316,806, 20.4.43. Appl. 14.3.41. Tube coupling.

H. G. Doll. U.S.P. 2,316,942, 20.4.43. Appl. 27.12.37. Apparatus for measuring temperature in bore-holes.

G. Miller. U.S.P. 2,316,967, 20.4.43. Appl. 24.6.41. Oil-base drilling fluid and method of regenerating the same.

G. Miller. U.S.P. 2,316,968, 20.4.43. Appl. 22.8.41. Oil-base drilling fluid containing air-blown asphalt.

W. F. Wingard. U.S.P. 2,317,010, 20.4.43. Appl. 25.7.40. Bore-hole deflecting tool in combination with a rotatable drill-bit.

A. S. Volpin. U.S.P. 2,317,122, 20.4.43. Appl. 11.6.42. Pump piston with flexible periphery.

H. G. Doll. U.S.P. 2,317,259, 20.4.43. Appl. 15.2.38. Device for determining the strata traversed by drill-holes.

C. Schlumberger and A. M. L. Doll. U.S.P. 2,317,304, 20.4.43. Appl. 11.5.35. Apparatus for electrical surveying of bore-holes.

J. E. Smith. U.S.P. 2,317,306, 20.4.43. Appl. 22.6.40. Rotary drilling rig for bore-holes.

G. L. Kothney. U.S.P. 2,317,386, 27.4.43. Appl. 14.3.42. Well-surveying instrument using electric current.

E. W. Rearwin. U.S.P. 2,317,404, 27.4.43. Appl. 16.11.40. Casing-head for a well through which a tubing may extend into the well.

C. A. Crowley and J. B. Mullen. U.S.P. 2,317,521, 27.4.43. Appl. 22.10.41. Sensitizer containing gel-forming colloidal clay.

T. B. Losey. U.S.P. 2,317,544, 27.4.43. Appl. 26.10.42. Coring-tool for side-wall coring.

L. C. Miller. U.S.P. 2,317,632, 27.4.43. Appl. 20.7.39. Means for surveying well-bores for inclination.

R. B. Booth. U.S.P. 2,318,284, 4.5.43. Appl. 27.3.41. Drilling mud containing migraine for viscosity control.

W. M. Burch. U.S.P. 2,318,370, 4.5.43. Appl. 6.12.40. Oil-well drilling-bit for rotary systems.

G. L. Kothney. U.S.P. 2,318,612, 11.5.43. Appl. 29.6.40. Well-surveying device with electric timing means.

D. G. Miller. U.S.P. 2,318,878, 11.5.43. Appl. 3.2.41. Open-hole tool-joint protector.

G. E. Nevill and A. L. Leman. U.S.P. 2,318,882, 11.5.43. Appl. 18.12.41. Ram construction for blowout preventers.

F. N. Osman. U.S.P. 2,318,885, 11.5.43. Appl. 18.12.41. Retriever shaped to be lowered into a well.

A. H. N.

Production.

801. Calculation of Load and Stroke in Oil-Well Pump Rods. B. F. Langer and E. H. Lamberger. *J. appl. Mech.*, March 1943, **10** (1), A1–A12.—The sucker-rod pump as used in oil-wells is treated as a problem in the longitudinal vibration of bars. Solutions are obtained for the forces and motions at both ends of the rod-string, thus giving formulæ for the calculation of polished-rod load and plunger travel. The results of the calculations are compared with test results. The conclusions may be summarized.

Peak polished-rod loads and effective plunger strokes in an oil-well can be calculated by using the following formulæ :

1. Complete formula for peak polished-rod loads :

$$PPRL = W_R\left[1 + \frac{ESK_1}{288L^2\delta_e}\right] + W_0\left[\frac{E_0\omega S_P}{144A_0L\delta_0}\right] + 2W_{OD} - W_{RB}.$$

2. Field formula for peak polished-rod load :

$$PPRL = W_R - W_{RB} + W_{OD} + 0{\cdot}75SN[17A_R \tan(0{\cdot}0004LN)^\circ + A_0].$$

3. Complete formula for effective plunger stroke :

$$EPS = \frac{S}{R} - \frac{24LW_{OD}}{E}\left[\frac{1}{A_R} + \frac{1}{A_T}\right].$$

4. Field formula for effective plunger stroke :

$$EPS = \frac{S}{\cos\,(0{\cdot}0004LN)^{\circ}} - \frac{W_{OD}L}{2(10^6)}\left[\frac{1}{A_R} + \frac{1}{A_T}\right].$$

The strokes and areas are expressed in inches; forces and weights in pounds; the well depth L in feet; and the pumping speed N in strokes/minute. These dimensions are commonly used in the oil-fields. Values of K_1 and of $1/R$ are given in graphs in the paper. W_R = weight of rod-string. E = Young's modulus of rod material. S = polished-rod stroke. δ_e = effective density of rod material = density corrected for weight of couplings, etc. W_0 = weight of full height of fluid column on net area of plunger. E_0 = Young's modulus of fluid column. ω = angular velocity of crank, rad./sec. S_P = plunger stroke. A_0 = velocity of sound in fluid. δ_0 = weight of fluid/unit volume. W_{OD} = differential fluid load = change in plunger force at end of stroke = load due to net fluid head on full area of plunger. W_{RB} = buoyant force on rods. A_R = area of rod cross-section. R = factor for calculating plunger travel, and A_T = area of cross-section of tubing wall.

The results calculated by the foregoing formulæ agree closely with test values obtained from a comprehensive test programme, carefully carried out on a single well. It is believed that data determined by tests made with similar care on wells at other depths, or under other operating conditions, will also closely agree with calculated values. Such comparisons are invited. A. H. N.

802. The Relationship Between Reynolds' Number and Velocity Distribution. L. S. Rhodes. *J. appl. Mech.*, March 1943, **10** (1), A21–A22.—It is shown that, for turbulent flow, the velocity distribution in the cross-section of a pipe, and the ratio of the mean velocity to centre velocity, depend on the rate of variation of the friction factor with Reynolds' number. The treatment is mathematical. A. H. N.

803.* Midcontinent Reconditioning Practices Entering New Era. Part 2. L. E. Elkins, R. H. Smith, L. F. Peterson, and P. P. Manion, Jr. *Oil Wkly*, 12.4.43, **109** (6), 18.—In this part of the paper the authors discuss the extension of both the vertical and lateral drainage areas of wells in order to increase their production. Horizontal extension by acidizing is studied in particular detail. The real acidizing problem in any treatment, and especially in reconditioning wells, is to determine in what part of the section the acid should go, and then to control it so that it will go there. If acid is merely pumped into a well, and especially one penetrating a section substantially depleted, it will enter the most permeable section, which is also the section most likely depleted. Thus, a great part of the acid may be spent in a section in which little or no good can be accomplished. Generally the increase in recovery from limestone sections with a varying permeability profile will be substantially credited to increasing permeability in the tighter zones. Directing acid to these zones may either reduce resistance to flow already established, or it may open a new channel to a porous zone not previously connected to the well-bore.

Consequently the first problem is to determine at least an approximate permeability profile. Core analysis and electrical logs, while of great value in sand-pools, are frequently inadequate for such a determination in limestone reservoirs. Drilling time, sample analyses, drill-stem tests, etc., offer some information as to this determination, but often such testing was not performed, and in many instances it was incomplete and inconclusive. A permeability profile can be measured on a well without having any test data obtained while drilling. Fluid input tests can be conducted by selective input tests using packers after calipering the well-bore for locating packer points. The ability of different parts of a pay-zone to take fluid is an index of permeability. Probably the simplest method involves the use of an acid service company's "electric pilot," which can be used to detect the depth of an oil-water interface in a well. This permits determining an accurate permeability profile with or without tubing in a well.

Once the permeability profile is determined, selective acidizing programmes may be designed. Case histories are presented as illustrations. A. H. N.

804. Formation Gas Used to Lift Oil in West Texas. H. F. Simons. *Oil Gas J.*, 29.4.43, **41** (51).—A well in which the gas from an upper formation is used to drive the oil from a lower sand to the surface is described. The gas-sand was 3386–3393 ft., and the oil-sand was 3401–3418 ft., with a subsidiary zone at lower depths. A formation packer was run on 2½-in. tubing to 3395 ft. just below the gas-producing zone. The 2½-in. tubing extended about 15 ft. below the packer, and beneath it was a 20-ft. accumulator chamber of 4-in. flush-joint pipe. The standing valve was landed at 3430 ft., and beneath it was a short, flat-bottomed anchor with slots to hold the gravel in place and still permit passage of the fluid.

At 3300 ft. a bottom-hole operating valve was installed in the tubing, with a conductor pipe below it inside the tubing and accumulator chamber. This valve admits gas from the annular space above the packer into, and downward through, tubing and accumulator chamber below the packer. It also permits upward passage through the fluid-conductor pipe and valve-ports into the tubing above the valve. A pack-off-type tubing head on the casing with the usual valves, which were kept closed, was used at the surface. The bottom of the fluid-conductor pipe is properly spaced with reference to the standing valve, so that the packer may be collapsed if desired.

The bottom-hole valve was operated through a Nixon surface-controlled intermitter, which consists of a timing device which lifts and lowers a weight-bar suspended on a wire. As long as the valve remains closed, gas is confined in the annulus, but as soon as the timing cycle raises the bar the valve opens, gas is admitted into the accumulator chamber, and the oil trapped there is forced upward through the conductor pipe, valve, and tubing to the surface. A. H. N.

805. Relationship Between Velocity, Oil Saturation, and Flooding Efficiency. R. C. Earlougher. *Petrol. Tech.*, May 1943, *A.I.M.M.E. Tech. Pub. No.* 1592, 1–11.—Two of the most important factors concerning the recovery efficiency in the production of oil from sandstone reservoirs by water-drive are percentage of oil saturation and velocity of the water-flood. From radial water-flushing of fresh core samples in the laboratory, and a study of field data of numerous water-flood projects in North-eastern Oklahoma, it appears that for any given oil saturation there is a critical maximum velocity above which the oil-recovery efficiency falls off very rapidly. In the case of the laboratory experiments, the efficiency was reported as the percentage of the total oil recovered from the core when the water passed was equivalent to 5000 brl./ft. When a water-flood is operated above the critical velocity the injected water–oil ratio rises extremely fast, thus shortening the economic life of the flood and reducing the ultimate oil recovery. The critical velocity apparently varies considerably with the percentage oil saturation of the sand, so that the higher the oil saturation at the beginning of a flood the higher the velocity which can be used successfully.

It is concluded that most of the failures among some of the earlier floods in the Mid-continent were due to two things: (1) too low an oil saturation, *e.g.*, 30%; and (2) too high water-injection rates. Although considerably more field data are required to establish definite limits, it would seem that the proper field injection rate for a 330 by 330 or 440 by 440-ft. spacing varies from approximately 1 brl./ft. of sand/day, where the oil saturation is as low as 30%, up to 5 brl./ft. of sand/day, when the oil saturation is as high as 45–50%.

In laboratory experiments it is essential that original interstitial water be taken into account. G. D. H.

806. Remedial Work in the Oil-fields of the Eastern Area of the United States. W. N. Little. *Petrol. Tech.*, *A.I.M.M.E. Tech. Pub. No.* 1596, 1–11.—Pattern water-flooding oil-sands in New York and Pennsylvania, especially in the Bradford third sand, is an effective way of securing maximum secondary recovery of oil. A large acreage of this Appalachian area is currently being converted into water-flood operation, and Fettke estimated that in 1940 60% of the Pennsylvania grade crude from this area was being produced by water-flooding. Horizontal drilling from a shaft is being attempted in Franklin County, Pennsylvania. Gas injection has been used in a number of fields, and pressure maintenance in the newer flush fields such as Louden gives indications of increasing primary recovery by 20–25% in some places.

The reconditioning methods used in the Appalachian fields include simple clean-cut, shooting, steaming, chemical treatment and acidization, and deepening. The methods of cutting and shooting a window are described in connection with opening upper zones. In most cases only zones that test as thieves are abandoned when new zones are opened, and the multiple zones are produced together and pumped from the deepest open formation.

It is easier and more economical to open an upper formation than a deeper one, and for the latter purpose cable tools are most often used unless there is much shale to be drilled. At Salem 104 wells have been deepened from the Devonian to the Trenton.

G. D. H.

807.* Development and Control of Oil Reservoirs. Part 1. S. E. Buckley and R. C. Craze. *Oil Wkly*, 3.5.43, **109** (9), 11. *Paper Presented before American Petroleum Institute.*—Recently a booklet, " Standards of Allocation of Oil Production," has been published summarizing present knowledge of production principles. This paper is a summary of the conclusions reached in the booklet. Oil-fields are divided into : (1) dissolved gas drive ; (2) gas-gap drive ; and (3) water drive. Each category is briefly discussed, and the chief characteristics and potentialities are given. The main questions in development are covered by :

(1) Enough wells must be drilled in any event adequately to explore and define the structure and to determine the gas- and water-levels. The only question involved in drilling, then, is the number of additional wells required and their spacing pattern. Money, labour, time, and materials spent in wells are largely irretrievable. It is not possible to back up from 5-, 10-, or 20-acre spacing. It is possible, however, to fill in from 40-, 60-, or 80-acre spacing, or any other exploratory pattern employed in outlining production. It seems obvious, therefore, that the prudent operator will not decide his ultimate well density in advance. He will drill as few additional wells as the conditions warrant, with the knowledge that he can fill in later should it prove necessary, rather than drill immediately as many wells as it is estimated can be afforded.

(2) In the matter of well completion, mistakes again will inevitably occur, but several simple considerations will cover most cases. (*a*) Wells should be completed in such manner as to exclude free gas and water. (*b*) Any well must take in sufficient producing section to yield oil at a reasonable rate. (*c*) Where this requirement does not conflict with requirement (*b*), it is good practice to open to production in a well only one separately identifiable producing horizon, thus providing for better subsequent control. The same result may in some cases be accomplished by multiple-zone completions. (*d*) Such purely mechanical details as whether to use screen, slotted-pipe, gravel-pack, or open-hole completion depend to a large extent on local sand conditions and have little or no bearing on reservoir performance.

The only remaining question is whether to complete wells in the top, bottom, or middle portion of a producing section. The proper position cannot be determined until the type of drive is known. Therefore the best completion is that which can most effectively and cheaply be changed when conditions warrant. In some areas casing cemented entirely through a producing section and perforated opposite a selected zone affords the best opportunity for successful later change of the producing interval.

A. H. N.

808.* Selective Shooting of Tight Sections Aids Stripper Wells. F. R. Cozzens. *Oil Wkly*, 3.5.43, **109** (9), 14.—The first step in selective shooting is to locate the tight sand and, if possible, to caliper it. The next step is to fill the hole with rubble rock, gravel, or some such material that can be easily drilled out. The hole is filled up to the base of the tight-sand section nearest the top of the pay. Tamping is done with the drill, so as to form a packed and even surface. A shell, filled with nitro-glycerine or gelatin, is run and seated on the surface of the packing material. The average nitroglycerine shell is the common 4½-in. type, allowing 3·4 quarts/each ft. of hole. Some operators substitute the less expensive gelatin, 90% strength, which seems to give somewhat better results in certain types of sand, especially conglomerate formations. The gelatin cartridges generally used are 4 × 16 in., which allows approximately 7·4 lb. for each foot of sand.

The shells must be long enough to extend from the bottom to the top of the selected zone. After the loaded shell has been seated properly, so as to prevent its being floated out of position, a heavy anchor or stemming (usually water) is turned into the well, the average amount being one barrel of water to each foot of shell. All shots are of the electric type—blasting-cap in shell, and water-proofed connections made to copper-wire line which extends up and out of the hole.

After the charge is exploded the well is cleaned and tested. A. H. N.

809.* Proper Installation of Hydraulic Pumping Equipment. K. C. Vaughn. *Oil Wkly*, 3.5.43, **109** (9), 28.—Hydraulic pumping experience has dictated several simple but essential pre-requisites for satisfactory operation. These are: (1) dehydration facilities to meet the required demands; (2) reserve oil to provide uninterrupted operation for short periods; (3) wax control; (4) a central power that will guarantee ample power oil and contant supply; (5) arrangement of facilities in order to simplify operations; and (6) a programme for training personnel in the operation of hydraulic pumps. These are discussed in some detail.

A typical installation is described. It consists of five engines and hydraulic pumps, not including charging pumps. A separate motor-driven charging pump provides oil for the entire setting. This choice was made to reduce maintenance by eliminating five individual pumps, ten belt-drives, counter-shafts, housing, etc. It was felt that power failures were so infrequent that separate power source would not be troublesome. A few features included in this power setting are: (1) Flanged and welded fittings and plug-valves throughout to reduce leakage from vibration. (2) Elimination of the spacer-block scavenger pump. All drainage from the space-block is by gravity to main drainage system. (3) Elimination of all individual pressure gauges and installation of a recording pressure gauge. This gauge is invaluable in studying operation and it can be seen from the clutch of each engine. (4) Installation of a mercoid-operated relay switch to shut down engines in case of oil-supply failure. (5) Installation of starters on each engine. Engines are started from batteries in the pumper's car by means of a cable and plug. (6) Presence of an oil-bath gas-fuel scrubber.

To encourage " good housekeeping " and facilitate repair, a cement floor surrounds the setting. Deep drainage-pits under each pump and a sloping apron help to keep the setting clean and orderly. Drain lines, gas-fuel lines, electrical conduits, and relief oil lines are under the floor. Only the suction and discharge lines are located on the surface. The well manifold provides convenient access to the pumper, and can be easily dismantled and assembled by production crews. Use of knockout collars assures practically the same spacing each time a pump is re-run, and the location of unions at convenient points speeds up maintenance work. Power-oil meters and production meters are located together near the road circling each location. A positive-type rotary flow-bean is used to control input oil rate, and its use is helpful in maintaining pump speeds at chosen points. Combined with a constant-discharge pressure, these beans provide a common basis for comparison. In practice pump speeds are often difficult to obtain, and the results are inconsistent. Any control method based on speed alone requires considerably more supervision and attention. A. H. N.

810. Use of Materials in Secondary Recovery. P. D. Torrey. *Oil Gas J.*, 6.5.43, **41** (52), 114.—*Paper Presented before American Petroleum Institute.*—Large but little-recognized secondary reserves which are available to augment the primary reserves exist in the United States. The development of these reserves usually involves a minimum of new materials, it being frequently possible to utilize existing production facilities and wells. Percentage increases in production from secondary-recovery operations correspond to the increase in production brought about by the active development of a new field.

Prevention of corrosion in both gas-repressuring and water-flooding operations will serve to eliminate frequent replacements of equipment, and will thereby provide substantial savings in new materials. The successful application of flowing methods in water-flooding operations eliminates the need for all surface and sub-surface equipment commonly required to lift oil to the surface.

Unitization can provide savings in material and in operating expense by reduction in the number of plants and pipe-lines. A. H. N.

811. Removal of Paraffin Accumulations in the University Field. B. C. Craft and R. F. Nichols. *Oil Gas J.*, 6.5.43, **41** (52), 124.—*Paper Presented before American Petroleum Institute.*—A new paraffin scraper, which has resulted in a substantial reduction in scraping time, is described. This tool has been used in the University oil-field, where it is good practice to scrape each well twice weekly. It is believed that the tool may also be used successfully on wells produced by a surface-controlled gas-lift system. The body consists of a ⅝-in. cold-rolled steel shaft, which is drilled with $\frac{3}{32}$-in. holes for the wires and tapped at right angles for Allen set-screws. The scratchers were made from 0·092-in.-diameter mild plough-steel wire, cut 2¼ in. long for 2½-in. tubing. The two semicircular knives at the top are made of spring steel, are sharpened on top and bottom edges, and provide an open passage for the flow of cut paraffin and well-fluid. For 2½-in. tubing the knives are 2¼ in. in diameter, and may be either welded or bolted to the steel bar.

This tool eliminates all the undesirable features of the circular knife or biscuit-cutter. The scratchers loosen and break the paraffin from the wall of the tubing into small chunks, and any accumulations remaining are removed by the overlapping circular knives. The paraffin is then, even at low rates of flow, carried up the tubing, with no danger of plugging the choke. It is believed that the combination of knives and scratchers more effectively cleans the tubing than the circular cutter, which leaves a thin layer of packed paraffin on the inside of the tubing. Wells, after being scraped with the latter, always cut harder than usual with the scratcher. A. H. N.

812.* Electric Pilot Promises Better Oil Recoveries. F. Briggs. *Oil Wkly*, 10.5.43. **109** (10), 13–16.—The device described is used to (1) determine a permeability profile of oil-wells; (2) spot or locate acid at any desired depth or for controlled use in any selected zone in the producing formation; (3) find the top of mud or other chemical bridges; (4) re-locate lost casing points or tubing bottom; and (5) determine the location of casing leaks.

Technically, the "electric pilot" is a fluid interface locater which causes an electric circuit to close upon submersion of this instrument in a conductive liquid or to break the circuit upon contact with a non-conductive medium or liquid. Simply, it is nothing more than a piece of apparatus lowered into the well by means of an insulated cable through which current will flow if the pilot is in (conductive) acid or salt water, and will not flow if it is in (non-conductive) oil. Thus, at the point where acid ends and oil begins, technically referred to as the "fluid interface," the pilot will only be lowered slightly into the conductive liquid before a current is noted, or raised slightly into the oil for the current flow to be broken. By holding the pilot electrode at the intermediate point of electrode contact, and knowing the depth of the pilot in the well, the interface is located.

The acid is pumped down the tubing, while the oil is introduced simultaneously into the tubing-casing annulus. In the case where selective acidizing is desired, the tubing is bottomed to the desired depth, the pilot seated in the tubing end, and acid entering from the surface passes through ports in the top of the pilot, down the hollow centre, and out through the perforated tail-piece. After passing through the pilot, which is suspended below the end of the tubing, the acid rises on the outside, and on reaching the first electrode, causes the electrical meter on the surface to show a half-scale deflection. On reaching the upper electrode, the acid face causes a full-scale deflection on the surface meter, thus indicating that the resistance connecting the two electrodes has been shorted out.

The use of the instrument to determine permeability profile and for other selective acidizing purposes is described. A. H. N.

813.* Development and Control of Oil Reservoirs. Part 2. S. E. Buckley and R. C. Craze. *Oil Wkly*, 10.5.43, **109** (10), 21.—*Paper Presented before American Petroleum Institute.*—The three types of drives—dissolved gas, gas cap, and water drives—outlined in Part 1 of the paper are further studied and methods of controlling reservoirs under each of these drives are discussed. After a long discussion, the general conclusion is that qualitatively it is easy to point out certain features of good and bad operation. The quantitative application to any specific field, however, is a complex and difficult matter, and the assumption that all fields are alike is both absurd and apt to be costly. It is imperative that each field be given individual and competent technical study. Furthermore, the technologist cannot invent facts. The more that is known about a specific reservoir, the better the resultant interpretation and control of its behaviour. Adequate information on the producing zone and its contents, on the production of oil, gas, and water, and on the reservoir pressure is particularly essential. Unless such data are complete and reliable, even the best technologist may be misled.

It should be readily apparent that efficient operation requires proper control of a whole reservoir, and not merely part thereof. Good practice on one lease and bad practice on another do not necessarily average out to give a reasonably efficient average. The question, then, may well be raised as to the manner in which an operator whose properties comprise only a small fraction of a field can see to it that the whole field is operated efficiently Obviously his only recourse is co-operation with other operators, in the acquisition and exchange of necessary engineering data and in the acceptance and promotion of common good practice. The incentive lies in the possible greater return at less cost. A. H. N.

814.* Dual Completions Are a Sound Production Practice. E. O. Bennett. *Oil Wkly*, 10.5.43, **109** (10), 33.—The paper is written as an answer to a paper on " Some Objections to Dual Completions " which recently appeared in *The Oil Wkly*, and here the author denies that multiple completion results in only a small saving of steel, and that it would disturb markets or constitute operating difficulties and hazards. The paper takes each paragraph of the previous article and analyses its implications. Thus it was stated that dual completions would completely upset present proration systems, and that the permitting of higher allowables to dually completed wells would require re-distribution of market demand, taking away from single-zone wells and fields and adding to dual or multiple-zone wells and fields. On the theory proposed in this argument no more wells of any type should be drilled anywhere, because each new well would be a liability against those already completed. An oil-well must be considered as a vertical pipe-line, simply providing a means of moving oil from a supply zone to the surface. Should there be more than one supply zone in overlying position under the same surface acreage, there can be no difference in the effect of moving oil or other hydrocarbons from the separate zones by two wells, one within the other (dual completions), than would exist were separate wells drilled to each horizon. The theory or idea advanced sounds like one that might be expected from an operator who owned only single-zone pools, and for this reason alone does not want the producer who may be fortunate enough to own acreage in multiple-zoned areas to enjoy the benefits of his rights and fortunes of his exploratory ability.

To illustrate the saving in steel, it is mentioned that in one area on the Gulf Coast the steel saved by the use of dual-completions over that required for two single wells to the same zones is approximately 120 tons. A. H. N.

815. Wax Distillate Used to Plug Channels in Pay-Zone. H. F. Simons. *Oil Gas J.*, 13.5.43, **42** (1), 47.—Among the methods devised for prevention, or cure, of channelling is the plugging of the permeable streaks with a substance which will be fluid at elevated temperatures and liquid at the formation temperature. In the Pennsylvania water-flood region, petroleum wax has been used in several instances. A variation of the same method is being tried out in two North Central Texas water-floods, and in this case residual fuel having a high wax content is employed. The operator doing this work has a water-flood in the Prideaux area of Archer County, and another near Alney in Young County.

The wax distillate was first heated to approximately 120° F. and then pumped into the producing formation, from 15 to 50 brls. being used in each injection well. Pressures up to 600 lb./sq. in. were employed in placing the wax-oil used for plugging. A cementing truck was used for handling the fuel oil after it had been heated. The accepted theory of the action of the wax distillate is that when heated it will enter the more permeable zones and travel a considerable distance before it cools and congeals and blocks the pores in the sand. The less permeable portions take very little of the heated oil, and it penetrates only a short distance into them. After it has congealed, very little water can pass through it, and hence the water-drive is directed into the less permeable portions of the formation which contains the bulk of the oil.
A. H. N.

816. Economics of Water-Flooding. D. P. Oak. *Oil Gas J.*, 20.5.43, **42** (2), 49–51. *Paper Presented before American Petroleum Institute.*—There are four major considerations which an operator must take into account in a proposed water-flood. They are: (1) an oil reservoir suitable to water-flooding; (2) source and supply of water; (3) source and supply of power; (4) marketing facilities. Engineering and economics are so closely related in studying these factors that it is difficult not to digress into an engineering discussion. Preliminary estimates on water-flooding are at best very uncertain, due to: (1) the impossibility of obtaining sufficient data on which to base an estimate without an investigation, which would practically amount to a development; (2) the changing technique in the operation of a water-flood. Water-flooding in the Midcontinent field is only 10 years old, and we are only beginning to get complete histories. In the meantime technique has so changed that the history of the early floods is of little value in estimating future recovery. Each item is briefly discussed. Finally, the economics of the project is discussed under (1) production expense, (2) water-system expense, and (3) overhead and administrative expenses. Grouping all these expenses and starting with a minimum of 2000 brls./acre—as any intensively developed pumping project having less recovery than that cannot be a financial success at the present time—experience has shown that over the life of a project production expense will vary from 15 to 30 cents, water expense from 10 to 20 cents, and true administrative expense from 5 to 10 cents/barrel of oil produced. Totalling these items gives a minimum of 30 cents and a maximum of 60 cents/brl. of oil, with the lower recovery projects usually going into the high-expense brackets. A. H. N.

817. Flowing *versus* Pumping Operations in Water-Flooding. T. Lawry. *Oil Gas J.*, 20.5.43, **42** (2), 52. *Paper Presented before American Petroleum Institute.*—Delayed drilling programmes are discussed. Then the advantages of flowing over pumping are discussed in some detail. The first advantage is simplicity of operation. Except for a few of the very deep water-flood projects which operate by gravity, all water-floods have a pressure plant to force the flooding water into the sand under pressure. If that plant can be made to serve the dual purpose of putting water into the ground and taking the oil out, the mechanical problems have been reduced to their simplest form. And that is just what flowing involves. Instead of the pressure head being entirely expended in the formation, as is the case in pumping, part of it is reserved to lift the oil and water from the bottom of the oil-well to the surface, thus eliminating the need for central powers and pumping jacks, or individual pumping units to do the work. All the arguments over flowing revolve around this point of whether it is cheaper to risk not getting as much oil by flowing, or to do the job the expensive way by pumping to get what is it hoped will be more oil than would be obtained by flowing.

Savings in man-power and material are further advantages. A new technique used in water-flooding, and one that is best adapted to flowing projects, is that of limited withdrawal, similar to that used in flush-fields under proration where the day's production is taken in a few hours or minutes and the well shut in again for the remainder of the 24-hr. period. In water-flooding, the oil-wells are drilled when 100% liquid saturation is attained, and as nearly simultaneously as possible, so that all wells are at peak production at one time. When all the wells have been drilled, the packers on the bottom of the tubing cemented in, and the wells capable of being shut in under pressure, the oil-wells are flowed wide open for 1 or 2 days, to determine the potential of the lease, after which some pre-established time or fraction of the day from 18 to 22 hrs. is taken as the daily quota. The gauge is given to all switchers as the amount to take from that lease, and no more. For a day or two it will take that long to get the oil, but soon the time will have been reduced by ½ hr., then by 1 hr., and so on until possibly only 12 hrs. will be needed to obtain what formerly required almost a full day. In the meantime the oil-wells are shut in and allowed to pressure up with the intake wells going along unhampered 24 hrs. a day. The theory of this procedure is discussed. A. H. N.

818. North Texas Operators Turning to Water-Flooding to Increase Oil Recovery. H. F. Simons. *Oil Gas J.*, 3.6.43, **42** (4), 35.—Projects in North Texas, and especially in the Prideaux district, are discussed. Practically all the leases were originally developed on a spacing of a little over 300 ft. between wells. The general plan is to five spot, with the injection wells being located in the centre of the four wells.

In contrast to a number of water-floods, the projects in the Prideaux area use water obtained from shallower wells for injection purposes. This has a number of advantages, the main one being that its chemical composition is constant, and consequently an adequate treatment can be designed. Lifting costs have not been found to be excessive. The water-zone is found at 350–400 ft., the water being lifted with jack and sucker rods operated from the central power through a rod-line. These water-wells are equipped with a 6-in. working barrel, 4-in. tubing, and ⅞-in. sucker rods. The oil-wells in the area do not produce salt water but a brackish water which is almost palatable. The water from the wells is pumped into a 1600-brl. wooden tank used as a reservoir. The tank is also equipped with a small aerating tower, over which the water passes. Some alum is added to eliminate the algæ, and the pH is controlled with hydrated lime. The water from the storage then passes by gravity through a 2 × 8-ft. filter filled with graduated gravel, sand, fine anthracite coal, and a blanket of ferric chloride coagulent. The filter is equipped with a float-control which keeps it full at all times. Finished water is stored in a 250-brl. tank. A wash-back line from the finished-water tank is connected through the pump to the filters. From two to eight filters are used, depending on the volume of water needed. The maximum injection pressure expected is less than 550 lb./sq. in., but the triplex pumps used are capable of a greater output. These pumps have an 8-in. stroke and either a 3½-in. or a 3-in. bore, and will handle 2000–3000 brls./day at 50 r.p.m. The pumps are generally equipped with brass pistons. Engines for driving the pumps range from 15–25 h.p.

Cleaning and other operational details are discussed. A. H. N.

819. Gravel Loading of Formation Increases Production of Jal Field Wells. H. F. Simons. *Oil Gas J.*, 10.6.43, **42** (5), 39–40.—A frequent difficulty in wells with a low fluid-level is the caving of the formation in the uncased portion of the hole, with the result that the hole is partly or completely plugged and the movement of oil into the well-bore reduced. Gravel packing, in which variegated rock material is placed between the hole and a liner, is a common remedy for this trouble. A New Mexico superintendent has developed a slightly different practice, in that the hole is simply loaded with gravel to a point above the caving section. The method is simple, quick, and inexpensive, and the resulting increase in production from the wells is very encouraging. The process was applied to a formation with three or four pay horizons totalling 40–50 ft. The lower portion of the uppermost pay-streak in the wells was shot, leaving a fairly large cavity. This pay-streak supplied only a portion of the production, and the oil from the lower zones must be obtained if maximum production is to be gained. The exposed unproductive formations have a tendency to cave and fill the space between the hole and the tubing, bridging it and shutting off part of the pay-zones. The wells were produced with the standing valve immediately above the bottom of the hole, but the cavings, fortunately, did not freeze the tubing. However, the bridge was sufficiently tight to keep the wells from obtaining the maximum production.

The first step in reconditioning is to pull the tubing and lifting equipment from the wells and clean them out to the bottom. The wells are also swabbed, to pull any loose material into the hole, where it can be bailed or sand-pumped out. If the hole does not cave too badly this part of the operation takes 3 or 4 days. After the hole is clean, the gravel is poured into it in 20-gal. increments. After each batch is trickled in, the tools are run to bottom to gauge the fill-up. This process is repeated until the hole has been filled to about 15 ft. above the top of the shot cavity. The approximate size of the shot-hold can be obtained by measuring the fill-up from each batch of gravel. The pea gravel used for this purpose consists of material not larger than ½ in. and not smaller than ¼ in. Its cost is approximately 6 dollars per yard, and the largest quantity used to load a hole to date is approximately 650 gal. About 18 hrs. is required to place the gravel.

After the gravel has been placed, the tubing and production equipment are run back in the hole, and operations started. The standing valve is, of course, located immediately above the top of the gravel, instead of opposite the lower-most pay-streak. Oil can get into the well-bore, and the formation pressure is sufficient to keep it standing above the top of the gravel-pack, where the lifting equipment can pick it up.

A. H. N.

820. Unitized Pressure Maintenance, Jones Sand Reservoir, Shuler Field, Arkansas. G. R. Elliott. *Oil Gas J.*, 10.6.43, **42** (5), 53.—The early development of the field and the coming into force of the field maintenance programme are briefly discussed, together with the geology of the field. Core analysis and associated data are presented graphically, and the significance of certain results is discussed. Graphs also illustrate the discontinuous nature of the permeability profile. Continuous shale or silty partings between permeable zones would cause the injected gas to move parallel to the bedding, and restrict its vertical movement; the discontinuous character of such separations in this reservoir provides extremely favourable conditions for the gas-cap type of pressure maintenance. The injected gas, instead of finding a short path to the nearest producing well, disperses in various directions and in various planes, resulting in more effective moving of oil to the well-bores.

Using the productive sand volume of nearly 150,000 acre ft. calculated from the isopach map, and applying 1·45 initial formation volume factor, the initial oil-in-place is calculated to be 106,000,000 brls. if 35% connate water is assumed, or 122,000,000 brls. if 25% connate water is assumed. The Jones sand was discovered 17th September, 1937, and to the end of 1942 had produced 25,550,000 brls. of oil. It is shown for a continuation of primary operation, an estimated recovery of 34,000,000 brls. (this represents 30% recovery of 113,000,000 brls.). Under unitized gas injection of 90% of the produced gas volume, it was estimated that the ultimate recovery would be approximately 20,000,000 brls. even though the secondary operations were not begun until one-half of the primary production had already been recovered. A. H. N.

821. Patents on Production. R. Bassinger. U.S.P. 2,317,021, 20.4.43. Appl. 5.2.40. By-pass and releasing means for connecting a conductor with a well-tool.

W. H. Ellinger. U.S.P. 2,317,038, 20.4.43. Appl. 25.4.41. Paraffin solvent for use in removing paraffin from tubing wall and containing a softener and bentonite.

G. H. Ennis. U.S.P. 2,317,039, 20.4.43. Appl. 25.9.39. Method and apparatus for determination of water leakages into wells.

P. M. Goodloe and H. G Berger. U.S.P. 2,317,050, 20.4.43. Appl. 3.5.41. Breaking petroleum emulsions of water-in-oil type.

M. B. Thomas. U.S.P. 2,317,121, 20.4.43. Appl. 2.11.40. Gas-lift intermitter.

J. L. Porter and I. R. Funk. U.S.P. 2,317,219, 20.4.43. Appl. 16.7.40. Production of petroleum using gas anchor in a pumping well.

M. Mennecier. U.S.P. 2,317,238, 20.4.43. Appl. 17.6.41. Gunfire control apparatus for gun perforators in wells.

A. Boynton. U.S.P. 2,317,356, 27.4.43. Appl. 28.11.38. Bellows-type slugging foot-valve for wells.

K. Boedeker and K. Winnacker. U.S.P. 2,317,726, 27.4.43. Appl. 22.11.38. Breaking agent for emulsions from crude petroleum and salt water and a breakage of said emulsions.

G. L. Thompson and L. A. Cejka. U.S.P. 2,318,029, 4.5.43. Appl. 24.1.40. Intermittent gas-lift pump.

T. B. Wayne. U.S.P. 2,318,034, 4.5.43. Appl. 6.7.37. Emulsion breaking compound containing the $\alpha\beta$-enal grouping ($-C=C-C=O$) and an unsaturated chemical body.

T. B. Wayne. U.S.P. 2,318,035, 4.5.43. Appl. 25.3.39. Process and reagent for resolving emulsions.

J. H. Wiggins. U.S.P. 2,318,134, 4.5.43. Appl. 7.12.39. Seal for floating tank-roofs.

J. H. Wiggins, U.S.P. 2,318,135, 4.5.43. Appl. 24.5.40. Seal for floating tank-roofs.

L. R. Knowlton. U.S.P. 2,318,167, 4.5.43. Appl. 4.10.40. Liner setting and washing device for wells.

R. C. Johnston. U.S.P. 2,318,315, 4.5.43. Appl. 6.2.40. Polish rod rotator for pumping wells.

E. Cooper. U.S.P. 2,318,466, 4.5.43. Appl. 17.11.41. Protecting apron for well-tubing.

W. J. Jones. U.S.P. 2,318,494, 4.5.43. Appl. 13.2.42 Surface rod-line jack for pumping wells.

L. R. Hodell and J. J. Heigl. U.S.P. 2,318,689, 11.5.43. Appl. 27.12.41. Tracing gas through underground formations.

H. J. Robertson and T. G. Wisherd. U.S.P. 2,318,714, 11.5.43. Appl. 24.1.40. Emulsion breaking by addition of aluminium chloride to oil-in-water types.

G. H. van Leeuwen. U.S.P. 2,319,020, 11.5.43. Appl. 18.9.36. Process for "impermeabilizing," tightening, or consolidating grounds and other earthy and stony masses and structures.
A. H. N.

Gas.

822.* **Helium.** A. H. Stuart. *Petroleum*, March 1943, **6** (3), 45.—The general properties and characteristics of helium are described. The chief source of production is from the natural gases associated with certain petroleum deposits, chiefly in Texas, Kansas, Oklahoma, Ontario, and Alberta. The amount of helium present in these gases varies from a fraction of 1% up to about 16%. Helium is isolated by fractional distillation from the liquefied gaseous mixture, and the ratio of the amounts of helium and nitrogen present in the gases is of great importance from the aspect of commercial production as well as the actual helium content. The cost of production of helium of 98% purity by this process at the plant in Texas was just under 12 dollars per 1000 cu. ft. when producing about 1 million cu. ft. per annum, which is about 3½% of its potential capacity. In the past the main use of helium has been for the inflation of dirigible aircraft. Its unique properties—*viz.*, inertness, high specific heat, and high coefficient of thermal conductivity—may, however, lead to considerable commercial demand for helium in post-war days. It has already proved successful in the fire-proofing of high-tension switch-gear, where rapid dispersal of heat and freedom from corrosion of contacts are of importance, and as an atmosphere for the sputtering of beryllium and aluminium, and for the annealing of bright metals. A steady but small demand existed up to the outbreak of war for use in electric-discharge lamps.
R. A. E.

Hydrogenation.

823.* Equipment and Control for the Determination of Catalytic Hydrogenation Rates. N. K. Anderson and C. A. Rowe. *Industr. Engng Chem.*, 1943, **35** (5), 554.—For industrial process design it is desirable to obtain reaction rate data under flow conditions, since kinetic data obtained from static systems may not be applicable. For the solution of problems of the foregoing types, a detailed description is given of a suitable piece of equipment. The description includes methods of measuring and controlling temperature, pressure, flow rates, and feed ratios. J. W. H.

824.* Determination of Catalytic Hydrogenation Rates. R. B. Beckmann, A. E. Pufahl, and O. A. Hougen. *Industr. Engng Chem.*, 1943, **35** (5), 558.—With the apparatus described by Anderson and Rowe (*ibid.*, p. 554) the reaction rates of the catalytic hydrogenation of *iso*-octene to *iso*-octane have been studied in the vapour phase under continuous-flow conditions with a nickel catalyst. Data are given for the reaction at 250° C. and 5 atmos. total pressure, and, from a correlation of the results, reaction rate equations are developed which show the effects of activated adsorption and surface reaction in terms of concentrations for two catalysts.
J. W. H.

Refining and Refinery Plant.

825.* Design of Solid Fluid Heat Exchangers. C. L. Lovell and G. Karnofsky. *Industr. Engng Chem.*, 1943, **35** (4), 391.—The data presented in this article are of value in estimating the heat transfer from gases to catalysts. Methods are given for solving

problems involving the transfer of heat under continuous parallel or counter-current conditions. To simplify the calculations graphical constructions are demonstrated.
J. W. H.

826.* Fractional Distillation of Binary Mixtures. Number of Theoretical Plates and Transfer Units. A. J. V. Underwood. *J. Inst. Petrol.*, **29** (234), 147.—The problem is treated mathematically. For binary mixtures with constant relative volatility the number of transfer units can be calculated in a form which readily permits of comparison with the number of theoretical plates required for the same separation. The computation can in both cases be greatly facilitated by using simple graphical method. Any separation with finite reflux can be exactly converted into an equivalent separation with total reflux by using a modified relative volatility and modified compositions.
A. H. N.

827.* Recent Developments in Welding. C. W. Brett. *J. Inst. Petrol.*, **29** (234), 157–162.—A well-illustrated paper on welding, metal-spraying, and other repair work in which molten metal is used, is presented. A process was recently perfected which made a clean sweep of most preconceived notions on the subject. It resulted in the achieving of a truly welded union with almost any combination of metals. This important fact is not generally realized, and so far only a few industries, among them the electrical trade in particular, have grasped its importance. Quite apart from repair work, for which the system was primarily evolved, its influence on new production will be potent, to say the least. Aluminium can be welded to steel if needs be, but however striking the dissimilarity between the two metals, tests to destruction, by exerting an increasing pull until something must break, always cause the weaker parent metal to fail first, whilst the weld invariably holds fast. A. H. N.

Chemistry and Physics of Hydrocarbons.

828. The Reaction of Epichlorohydrin with the Grignard Reagent. J. K. Magrane, Jr., and D. L. Cottle. *J. Amer. chem. Soc.*, 1942, **64**, 484–487.—The alkoxide from either epichlorohydrin and magnesium bromide, or from 1-bromo-3-chloro-2-propanol and ethyl magnesium chlorobromide, gave ethane, ethylene, and a product with the properties expected of *cyclo*propanol on reacting with ethyl magnesium bromide. This supports the theory that ethylene oxides react spontaneously with both the alkyl magnesium and magnesium bromide bonds.

Epichlorohydrin with ethyl magnesium bromide direct also gave a product that appeared to be *cyclo*propanol. E. H. W.

829. Hydrogenation of Alkyl Phenyl Ketones in the Presence of Copper Alumina Catalysts. V. N. Ipatieff and V. Haensel. *J. Amer. chem. Soc.*, 1942, **64**, 520–521.—A copper-aluminium catalyst containing 2·5–8% Al_2O_3 (on the reduced basis) has been found to hydrogenate ketones without affecting the benzene nucleus. A number of *n*-alkyl phenyl ketones were thus hydrogenated at 115° C., producing *n*-alkyl phenyl carbinols, and it was shown that butyrophenone and valerophenone were more difficult to hydrogenate than any of the other *n*-alkyl phenyl ketones tried. Using the same catalyst, the carbinols could be converted at 150–180° C. into the corresponding alkyl benzenes, giving yields of 95–98%. E. H. W.

830. An Acetylenic Analogue of Neopentyl Bromide; Evidence that the Hindrance to Displacement Reactions in Neopentyl Halides is Steric in Nature. P. D. Bartlett and L. J. Rosen. *J. Amer. chem. Soc.*, 1942, **64**, 543–546.—1-Bromo-4 : 4-dimethylpentyne-2 showed no sign of hindrance compared with 1-bromo-heptyne-2, in exchange reactions with potassium iodide in acetone solution. The rates of reaction of other related bromides treated with potassium iodide in acetone solution are also given. From the results it is concluded that the hindrance effect shown in neopentyl alcohol and halides is steric rather than chemical. Space models of neopentyl compounds and the reactivities of the compounds studied also support the above conclusion.
E. H. W.

831. Vapour Pressures and Critical Constants of *iso*Butene. J. A. Beattie, H. G. Ingersoll, and W. H. Stockmayer. *J. Amer. chem. Soc.*, 1942, **64**, 546–548.—Measurements of the vapour pressure of *iso*butene between 30° C. and 125° C. are given. Good agreement was obtained between the observed vapour pressures and calculated values from a two-constant equation. Critical constants determined by the compressibility method were : $t_c = 144{\cdot}73 \pm 0{\cdot}05°$ C. (Int.) ; $p_c = 39{\cdot}48 \pm 0{\cdot}05$ normal atmosphere ; $v_c = 0{\cdot}240$ litre/mole (4·28 c.c./g.) ; $d_c = 4{\cdot}17$ mole/litre (0·234 g./c.c.). The uncertainty in the critical volume and density is 1%. Benedict's results for critical pressure and temperature, obtained by the disappearance of the meniscus method, are in good agreement with those given above. E. H. W.

832. The Compressibility of and an Equation of State for Gaseous *iso*Butene. J. A. Beattie, H. G. Ingersoll, and W. H. Stockmayer, *J. Amer. chem. Soc.*, 1942, **64**, 548–550.—Compressibility measurements of gaseous *iso*butene from 150° C. to 275° C. and from a density of 1·0–9·0 mole/litre are reported, the maximum pressure being 250 atm. Polymerization of the *iso*butene in a glass-lined bomb did not seriously affect the compressibility determinations below 275° C. Constants for the Beattie–Bridgeman equation of state were determined from the data up to the critical density, and the calculated and observed pressures are compared. Calculated values of the second virial coefficient are also given from 150° C. to 275° C. E. H. W.

833. Polyphenylnaphthalenes. I. 1 : 2-Diphenylnaphthalene. F. Bergmann, H. E. Eschinazi, and D. Schapiro. *J. Amer. chem. Soc.*, 1942, **64**, 557–558.—A synthesis of 1 : 2-diphenylnaphthalene is described. Starting from α-phenyl-β-benzoylpropionic acid, a two-stage reduction process gave α, γ-diphenyl butyric acid. This on cyclization by a Friedel–Crafts reaction gave a tetralone which, with phenyl magnesium bromide, produced 1 : 2-diphenyl-3 : 4-dihydro-naphthalene, and the latter compound was then dehydrogenated to 1 : 2-diphenylnaphthalene by the addition of lithium. E. H. W.

834. Polyphenylnaphthalenes. II. 1 : 2 : 3-Triphenylnaphthalene. F. Bergmann, D. Schapiro, and H. E. Eschinazi, *J. Amer. chem. Soc.*, 1942, **64**, 559–561.—1 : 2 : 3-Triphenylallyl-sodium with carbon dioxide, then hydrogenation, gives α, β, γ-triphenylbutyric acid. A tetralone derivative is then obtained which, with phenyl magnesium bromide, gives 1 : 2 : 3-triphenyl-3 : 4-dihydronaphthalene and on dehydrogenation gives 1 : 2 : 3-triphenylnaphthalene. E. H. W.

835. The Decomposition of Certain Acetylenic Carbinols. A. F. Thompson, Jr., and C. Margnetti. *J. Amer. chem. Soc.*, 1942, **64**, 573–576.—The preparation and properties of a number of acetylenic tertiary carbinols are described. These carbinols were then decomposed over commercial alumina. A simple dehydration takes place with alkylethynyl substituents, but ethynyl and phenylethynyl substituents yielded the acetylenic hydrocarbon and the ketone. In aqueous potassium hydroxide solution the cleavage of the acetylenic group occurs generally for all the hydrocarbons investigated. E. H. W.

836. Alkyl Carbonates in Synthetic Chemistry. III. Condensation with Nitriles. Synthesis of α-Cyano Esters. V. H. Wallingford, D. M. Jones, and A. H. Homeyer. *J. Amer. chem. Soc.*, 1942, **64**, 576–578.—Aliphatic nitriles and aryl acetonitriles, on treating with sodium or potassium alcoholate in a large excess of alkyl carbonate, yielded α-cyano esters. Lower members of the aliphatic series gave poor yields, and unsaturated compounds tended to give tars. E. H. W.

837. Alkyl Carbonates in Synthetic Chemistry. IV. Alkylation of Malonic Esters by Alkyl Carbonates. V. H. Wallingford and D. M. Jones. *J. Amer. chem. Soc.*, 1942, **64**, 578–580.—Ethyl, butyl, *iso*butyl, *iso*amyl, and benzyl groups were introduced by the corresponding carbonates into the metal derivatives of a variety of malonic esters. Malonic ester itself was not alkylated, but mono-substituted malonic esters were successfully alkylated for any chain-length provided it was a primary aliphatic group.

Poor yields were obtained using secondary carbonates, and also if the substituent of the malonic ester was a secondary aliphatic group, but good yields were obtained with phenyl- and benzyl-substituted malonic esters. E. H. W.

838. Alkyl Carbonates in Synthetic Chemistry. V. Alkyl Carbonates as Solvents for Metalation and Alkylation Reactions. V. H. Wallingford, M. A. Thorpe, and A. H. Homeyer. *J. Amer. chem. Soc.*, 1942, **64**, 580–582.—Metalation and alkylation of malonic esters, β-keto esters and α-cyano esters has been successfully accomplished, using alkyl carbonates as reaction media. In this way formation of the metal derivative is completed without cleavage by alcoholysis taking place. The preparation is reported of several new malonic esters, including some containing two *s*-butyl groups which have previously been unobtainable by usual methods. E. H. W.

839. Brucine as a Reagent for Partially Resolving Bromoalkanes; the Configurations of some Diastereomeric Dibromoalkanes. H. J. Lucas and C. W. Gould, Jr. *J. Amer. chem. Soc.*, 1942, **64**, 601–603.—Using brucine, and under identical conditions, one isomer of dibromoalkane becomes optically active, while the other does not. This partial resolution is due to a difference in the rates with which antipodal dibromoalkanes react with brucine. The effect of adsorption was negligible. There was no conversion of a *dl*- to a *meso*-form or *vice versa* with 2 : 3-dibromobutanes, 3 : 4-dibromohexanes, or 4 : 5-dibromo-octanes. The *dl*-isomer when treated with brucine becomes optically active, while the *meso*-form does not. Configurations previously assumed for these symmetrical dibromoalkanes are confirmed. E. H. W.

840. Reactions with Tetraphenyl*cyclo*pentadienone. Condensation with Cyclic 1 : 3-Diene Systems. O. Grummit, R. S. Klopper, and C. W. Blenkhorn. *J. Amer. chem. Soc.*, 1942, **64**, 604–607.—Tetraphenyl*cyclo*pentadienone would not condense with furan, pyrrole, N-methyl-pyrrole, or thiophene. With *cyclo*pentadiene an addition product was obtained containing one molecule of each of the reactants. From a series of reactions the compound formed was inferred to be 4 : 7-endocarbonyl-8 : 9-dihydroindene. It is suggested that the lower resonance energy of *cyclo*pentadiene compared with the other compounds tried is the reason for its reaction with tetraphenyl*cyclo*pentadienone. E. H. W.

841. Kinetics of the Hydrogen Fluoride Catalyzed Reaction between Toluene and *t*.-Butyl Chloride. J. W. Sprauer and J. H. Simons. *J. Amer. chem. Soc.*, 1942, **64**, 648–659.—This paper presents a study of the kinetics of the reaction between toluene and *t*.-butyl chloride when catalysed by hydrogen fluoride, the course of the reaction being followed by measurement of the hydrogen chloride evolved. The reaction is homogeneous, and proceeds at a measurable rate at 25° C., and it is of first order with respect to *p*-*t*.-butyl chloride, which is produced quantitatively under a wide range of conditions. The reaction is approximately proportional to the 5·5 power of the hydrogen fluoride pressure. Oxygen had no catalytic effect, but small amounts of water or methyl alcohol had very marked accelerating effects. From the results a detailed discussion of the possible mechanisms of the reaction is given. E. W. H.

842. Halogen Addition to Ethylene Derivatives. I. Bromine Additions in the Presence of Bromide Ions. K. Nozaki and R. A. Ogg, Jr. *J. Amer. chem. Soc.*, 1942, **64**, 697–704.—The equilibrium constant for the dissociation of potassium tribromide in glacial acetic acid has been determined at three temperatures. A study was made of the action of bromine in the presence of lithium bromide on maleic and fumaric acids. The initial products were dibromides, which could only be accounted for by a *trans*-addition. Rate measurement data fitted best the rate expression :

$$-\frac{d(\mathrm{Et})}{dt} = k_a[\mathrm{Br}_3^-][\mathrm{Et}] = \frac{k_a}{K}[\mathrm{Br}_2][\mathrm{Br}^-][\mathrm{Et}]$$

where [Et] represents the concentration of the ethylene derivative. The rate of reaction was higher in solutions of low ionic strength. Addition of other salts as well as lithium bromide retarded the reaction, indicating this retardation to be a salt effect.

A much better catalyst than lithium bromide for the addition of bromine to maleic and fumaric acids was found to be hydrobromic acid, The same rate expression was followed, but the rate of reaction was proportional to the concentration of proton doners. While neither light nor oxygen had any effect on the lithium-bromide or hydrobromic-acid-catalysed reactions, added water retarded the latter reaction to a greater degree. The addition of bromine to vinyl bromide in glacial acetic acid was studied kinetically. This reaction was also catalysed by lithium bromide, and the same rate expression satisfied when the concentration of bromide ions was much higher than that of bromine. The reaction was not affected by the ionic strength of the solution or the concentration of proton doners, in contrast with the corresponding reactions with maleic and fumaric acids, thus verifying the authors' suggestion that these latter effects were due to the presence of the carboxyl group. The same catalytic effect was shown by hydrobromic acid and lithium bromide in the action of bromine on allyl chloride. With allyl acetate, hydrobromic acid showed a somewhat better catalytic effect; the difference between the two catalysts, however, was much less marked than with maleic and fumaric acids. E. H. W.

843. Halogen Addition to Ethylene Derivatives. II. The Mechanism of the Halide Ion Catalysed Addition Reactions. K. Nozaki and R. A. Ogg, Jr. *J. Amer. chem. Soc.*, 1942, **64**, 704–708.—In nearly all previous studies of halogen addition to ethylene derivatives the halogen molecule and halide ion were from the same element. This paper reports the effects of other ions, some not halides, all in glacial acetic acid as solvent. Bromine and vinyl bromide react autocatalytically, but addition of lithium bromide causes a greatly increased consumption of bromine. The kinetic data conformed best to the rate expression $-\frac{d(\mathrm{Et})}{dt} = k[\mathrm{Br}_2][\mathrm{Cl}^-][\mathrm{Et}]$, where Et represents the ethylene derivative, *i.e.*, vinyl bromide. The reaction was of first order with respect to the concentrations of vinyl bromide, bromine, and lithium chloride. Bromine addition to allyl chloride was catalyzed by acetate, bisulphate, and nitrate ions, as well as halide ions, but cations had no effect. Addition of iodine to allyl chloride was also catalysed by electrolytes.

Mechanisms of the halide catalysed reactions are discussed. The one giving better correlation with experimental facts involves a termolecular reaction between the unsaturated compound, the halide ion, and the halogen molecule.

Preliminary complexes may be formed between the ethylene derivative and the halide ion, but it is suggested that in general the addition to the double bond occurs by simultaneous and joint action of the halide ion and the halogen molecule. In some cases, however, association between the ethylene derivative and either the halide ion or halogen molecule may precede a reaction with the other molecule. E. H. W.

844. Halogen Addition to Ethylene Derivatives. III. Bromine and Iodine Additions in Glacial Acetic Acid. K. Nozaki and R. A. Ogg, Jr. *J. Amer. chem. Soc.*, 1942, **64**, 709–716.—The reaction of bromine with allyl chloride in glacial acetic acid is shown to be complex, by the mixture of products and by the rate expression:

$$\frac{-d(\mathrm{Et})}{dt} = k_a[X_3^-][\mathrm{Et}] + k_b[X_2][\mathrm{Et}] + k_c[X_2]^y[\mathrm{Et}] \quad . \quad . \quad . \quad . \quad (1)$$

where Et represents the ethylene derivative, *i.e.* allyl chloride, X represents the halogen, and $y > 2$. The results of kinetic studies at three temperatures are given. The reaction was extremely sensitive to added water, but was unaffected by packed reaction vessels or atmospheres of oxygen or carbon dioxide. Addition of bromine or iodine to allyl acetate gives rise to similar reactions which require an analogous rate expression and which have similar characteristics. The action of iodine on allyl alcohol was shown to be even more complex, being of a higher order than the second with respect to iodine, and of higher order than the first with respect to allyl alcohol concentration. A detailed discussion is given of the mechanisms of these halogen addition reactions. Each of the three right-hand terms in the rate expression (1) are taken to represent a different addition process, and each is discussed separately. The first term corresponds to the halide ion catalysed reaction (see previous abstract). The second term has been assumed to correspond to a reaction in which a haloacetate and hydrogen halide are produced. Results presented in this paper indicate that a reaction probably of third or higher order with respect to halogen concentration is involved. This reaction is represented by the third term in the expression. Conflicting results reported in the literature are explained on the basis of this complex rate expression. E. H. W.

845. Magnetic Susceptibilities of *Cis*- and *Trans*-Decalin. Note by W. Byerly and P. W. Selwood. *J. Amer. chem. Soc.*, 1942, **64**, 717–718.—Magnetic susceptibilities of *cis*- and *trans*-decalin at 35° C. are reported as: $-0{\cdot}774 \times 10^6$ and $-0{\cdot}779 \times 10^6$ respectively. The significance of the small difference between the two values is discussed. E. H. W.

846. 1 : 2-Diphenyl-3 : 4-dihydronaphthalene. Communication from H. M. Crawford. *J. Amer. chem. Soc.*, 1942, **64**, 727–728.—Melting points of the compound obtained by Bergmann *et al.* (*J. Amer. chem. Soc.*, 1942, **64**, 557) have been compared with the same compound from a different preparation by this author.

The explanation of the difference in the two melting points is suggested to be due to the fact that the two compounds are physical isomers, one of a high-melting form and the other a low-melting form. E. H. W.

847. The Action of Hydrogen Fluoride, Sulphuric Acid, and Phosphoric Acid on Optically Active 2-Butanol. R. L. Burwell, Jr. *J. Amer. chem. Soc.*, 1942, **64**, 1025–1031.—With sulphuric acid, racemization of optically active 2-butanol proceeds more rapidly than dehydration, polymerization, or alkylation. The racemization with equimolecular mixtures is of the first order with respect to the alcohol, but decreases with increasing concentrations of water. The general action of hydrogen fluoride is similar, but a much larger acid–alcohol ratio is needed.

It is suggested that, partly because of its lower activity, phosphoric acid produced only slight racemization under any of the conditions studied. E. H. W.

848. The Alkylation of Benzene in the Presence of Acid Catalysts. R. L. Burwell, Jr., and S. Archer. *J. Amer. chem. Soc.*, 1942, **64**, 1032–1034.—This paper describes the alkylation of benzene by optically active *s.*-butyl alcohol in the presence of hydrofluoric, sulphuric, and phosphoric acids, and also boron trifluoride. *s.*-Butyl benzene was produced showing rotations of opposite signs to those of the original alcohols. E. H. W.

849. The Heat Capacity and the Vapour Pressure Hysteresis in Liquid *iso*Pentane. Isomers due to Hindered Rotation. J. G. Aston and S. C. Schumann. *J. Amer. chem. Soc.*, 1942, **64**, 1034–1039.—In this paper a graph is given of the heat-capacity data obtained on liquid *iso*pentane between 180° K. and 240° K. Points are given for more than twenty various treatments of the sample. Hysteresis effects have been found, both in the heat capacity and also in vapour-pressure measurements, these effects being about 100 times the precision of the instrument. The authors suggest the slow transfer of one isomeric form into another made possible by restricted rotation as an explanation of these results. E. H. W.

850. The Heat Capacity and Entropy, Heats of Fusion and Vaporization, and the Vapour Pressures of *iso*Pentane. S. C. Schumann, J. G. Aston, and M. Sagenkahn. *J. Amer. chem. Soc.*, 1942, **64**, 1038–1043.—This work is a continuation of that reported in the preceding abstract, and the material used, method, and accuracy are the same as for that paper. Heat-capacity measurements are given between 20° K. and 290° K., vapour pressures between 217° K. and 290° K. The melting point, normal boiling point, heats of fusion, and vaporization are also reported. From an empirical equation for vapour pressure calculated values for boiling point and heat of vaporization are given. The molal entropies in the liquid and gas state are also calculated.

The free energies of neopentane, *iso*pentane, and *n*-pentane at 298° K. calculated from this and other work are tabulated. E. H. W.

851. Ketene Acetals. IX. Ketene Dialkylacetals. S. M. McElvain and P. M. Walters. *J. Amer. chem. Soc.*, 1942, **64**, 1059–1060.—The preparation and properties of ketene di-*n*-propyl-, di*iso*butyl-, and di*iso*amyl-acetal are recorded. The properties of the

compounds prepared by Schrieber and his collaborators (*Ann.*, 1927, **458**, 21), and claimed to be the same as the above ketene acetals, are shown to be different.
E. H. W.

852. Certain Derivatives of the Octadecenoic Acids. I. The *p*-Phenylphenacyl Esters. II. The *S*-Benzylthiuronium Salts. J. P. Kass, J. N. Nichols, and G. O. Burr. *J. Amer. chem. Soc.*, 1942, **64**, 1061–1062.—The *p*-phenylphenacyl esters of oleic, elaidic, linoleic, linolelaidic, linolenic, β-eleostearic, and α-tetrabromostearic acids were prepared. The melting points were satisfactory, but among the unsaturated derivatives, only the already known esters of the first two acids mentioned gave iodine numbers agreeing with the calculated values. For various reasons, none of the *S*-benzylthiuronium salts of any of the above acids was suitable for identification purposes.
E. H. W.

853. The Utilization of Aliphatic Nitro-Compounds. III. Nitroalcohols Prepared from Aldehydes Containing No Other Functional Group. C. A. Sprang and E. F. Degering. *J. Amer. chem. Soc.*, 1942, **64**, 1063–1064.—The preparation and some physical constants of twenty nitro-alcohols are reported.
E. H. W.

854. Alkanolamines. XI. Monoalkylamino Alcohols and their Esters. C. B. Kremer and E. Waldman. *J. Amer. chem. Soc.*, 1942, **64**, 1089–1090.—The preparation of a series of new monoalkylamino-alcohols and their *p*-nitrobenzoates is reported.
E. H. W.

855. Addition Polymerization Catalysed by Substituted Acyl Peroxides. C. C. Price, R. W. Kell, and E. Krebs. *J. Amer. chem. Soc.*, 1942, **64**, 1103–1106.—Polystyrene and polymethyl methacrylate prepared in the presence of chloroacetylperoxide, *p*-bromobenzoylperoxide, or anisoylperoxide, contained on the average from a half to two and a half groups derived from the peroxide per polymer molecule. These results support the suggestion that free radicals from the thermal decomposition of the peroxide catalysts initiate the polymerization.
E. H. W.

856. Branched-Chain Fatty Acids. I. Synthesis of 17-Methyloctadecanoic Acid. J. Carson. *J. Amer. chem. Soc.*, 1942, **64**, 1106–1110.—The reaction of an alkyl cadmium compound with the acid chloride of a half ester has been used successfully in this synthesis of 17-methyloctadecanoic acid. This work begins a proposed series of syntheses of methyl-stearic acids.
E. H. W.

857. A New Method of Synthesizing Aliphatic Difluorides. M. W. Renoll. *J. Amer. chem. Soc.*, 1942, **64**, 1115–1116.—The paper describes the synthesis of five aliphatic difluorides, from butane to octane, by the action of monochloro-olefins and anhydrous hydrogen fluoride under pressure at moderate temperature. Physical properties of three new compounds, $C_2H_5CF_2C_2H_5$, $CH_3CF_2CH_2CH(CH_3)_2$, and $CH_3CF_2(CH_2)_5CH_3$, are given.
E. H. W.

858. The Cleavage of Ethers with Boron Bromide. I. Some Common Ethers. F. L. Benton and T. E. Dillon. *J. Amer. chem. Soc.*, 1942, **64**, 1128–1129.—When cleaved by boron bromide, simple alkyl ethers yielded alcohols and alkyl bromides, while mixed alkyl phenyl ethers yielded phenols and alkyl bromides. Further work on the action of boron bromide on ethers is proceeding.
E. H. W.

859. The Structures of Methylene*cyclo*butane and Hexamethylethane. S. H. Bauer and J. Y. Beach. *J. Amer. chem. Soc.*, 1942, **64**, 1142–1147.—Although configurations of these two compounds are known from chemical data, this investigation by electron diffraction was made to verify the accepted structures.

The results were: (*a*) Methylene*cyclo*butane carbon atoms are co-planar, four of them on the average at the corners of a square with (1·56 ± 0·03 Å. on the side) and the fifth on an extension of one of the diagonals (1·34 ± 0·02 Å. from the carbon atom in the ring), (*b*) Hexamethylethane c–c distances are all 1·54 ± 0·02 Å., with the exception of the central c–c distance, which is probably 1·58 ± 0·03 Å. Carbon valence angles are 111 ± 2°; C–H = 1·09 Å. was assumed. E. H. W.

860. The Preparation and Directed Chlorination of 1 : 1 : 1-Trifluoropropane. A. L. Henne and A. M. Whaley. *J. Amer. chem. Soc.*, 1942, **64**, 1157–1159.—$CH_3CH_2CCl_3$ would not yield $CH_3CH_2CF_3$ by halogen exchange owing to loss of hydrogen chloride. A successful synthesis was accomplished starting from $CH_3CH = CCl_2$ (prepared from readily available material) which yielded the desired product by halogen exchange. $CH_2ClCH_2CF_3$, $CHCl_2CF_3$, $CCl_3CH_2CF_3$, and $CCl_3CCl_2CF_3$, were successively yielded by chlorination of $CH_3CH_2CF_3$ in sunlight, thus verifying the strongly directing effect of fluorine. No evidence for a tetrachloride was found, the chlorination proceeding directly from a trichloride to a pentachloride. A list of new fluorochloropropane derivatives with their physical properties is given, and also the verifications of their formulæ. E. H. W.

861. The Dipole Moment of a Free Radical. J. Turkevich, P. F. Oesper, and C. P. Smyth. *J. Amer. chem. Soc.*, 1942, **64**, 1179–1180.—Dipole measurements of α, α-diphenyl-β-picryl hydrazine, and of the free radical, α, α-diphenyl-β-picrylhydrazyl have been measured. The results are discussed and compared with previous readings. E. H. W.

862. Raman Spectra of some Aromatic Carbonyl and Nitro-Compounds. M. J. Murray, F. F. Cleveland, and R. H. Saunders. *J. Amer. chem. Soc.*, 1942, **64**, 1181–1184.—Raman frequencies, estimated intensities, and depolarization factors are reported for acetophenone, mesitylaldehyde, acetylmesitylene, methyl-2 : 4 : 6-trimethylbenzoate and 2 : 4 : 6-trimethylbenzoyl chloride.

Three new lines are reported for acetopheone, the only compound of this series on which previous results were known to the authors. E. H. W.

863. Catalytic Addition Reactions of Acetylenic Alcohols. G. F. Hennion and W. S. Murray. *J. Amer. chem. Soc.*, 1942, **64**, 1220–1222.—The actions of methanol and acetic acid with dimethylethynl-carbinol in the presence of mercuric oxide and boron fluoride are reported in *J. Amer. chem. Soc.*, 1940, **62**, 653. It has now been shown that representative acetylenic alcohols condense with (*a*) methanol to form a number of substituted dioxanes, (*b*) ethylene glycol to form various dioxolanes, and (*c*) acetic acid to give acyloin acetates.

Physical constants, yields, and analytical data for the products obtained are given. E. H. W.

864. The Heat Capacity of Organic Vapours. III. Nitromethane. Note by T. de Vries and B. T. Collins. *J. Amer. chem. Soc.*, 1942, **64**, 1224–1225.—These authors report heat-capacity data for nitromethane which shows excellent agreement with the results of Pitzer and Gwinn (*J. Amer. chem. Soc.*, 1941, **63**, 3313). E. H. W.

865. Mechanical Properties of Substances of High Molecular Weight. II. Rigidities of the System Polystyrene–Xylene and their Dependence on Temperature and Frequency. J. D. Ferry. *J. Amer. chem. Soc.*, 1942, **64**, 1323–1329.—Solutions of polystyrene in xylene will support transverse vibrations and therefore possess rigidity. The propagation of transverse vibrations through solutions ranging from 15·3 to 52·3% polymer at temperatures of −5 to 40° C. and frequencies between 200 and 4000 cycles have been studied. Dispersion and damping effects are described and from the observations was obtained a relaxation time of about 4×10^{-4} sec., this was independent, to a first approximation, of temperature and concentration.

The modulus of rigidity was calculated from the velocity of wave propagation, and in the range studied varied between 10^4 and 10^6 dynes/cm.$^{-2}$. The results are discussed in terms of the molecular behaviour of long-chain polymers. E. H. W.

866. Mechanical Properties of Substances of High Molecular Weight. III. Viscosities of the System Polystyrene–Xylene. J. D. Ferry. *J. Amer. chem. Soc.*, 1942, **64**, 1330–1336.—At temperatures between 1° C. and 30° C. the viscosities of solutions of

15·4–52·3% polystyrene in xylene have been measured in a Stormer viscosimeter. The dependence of the viscosity on shearing stress, temperature, and concentration is described and discussed. More concentrated solutions showed elastic recoil. From the data, information was obtained on a modulus of rigidity representing recoverable deformation under steady flow and a time function related to a relaxation function. Viscosity and rigidity data from this and the previous paper are interpreted by two molecular mechanisms. The first mechanism is associated with a modulus of rigidity of the order of 104 dynes/cm.$^{-2}$, which is proportional to the concentration (up to 30%), and a mean relaxation time which varies with the concentration and is roughly proportional to the macroscopic viscosity. This mechanism is postulated to be the uncurling of flexible molecules. In the second mechanism the modulus of rigidity is proportional to the third power of the concentration (up to 30%) and the relaxation time is independent of concentration, and hence viscosity. The suggestion is made that this second mechanism is connected with the bending of carbon–carbon bonds.

E. H. W.

867. Reactions of Bromine with Carbon Tetrachloride and Tetrachloroethylene Following Neutron Capture and Isomeric Transition. E. G. Bohlman and J. E. Willard. *J. Amer. chem. Soc.*, 1942, **64**, 1342–1346.—A bromine atom which is recoiling from the emission of a γ-ray emitted as a result of neutron capture has about the same probability of reacting with liquid carbon tetrachloride as a bromine atom which has just undergone isomeric change. Practically no reaction occurs in the gas phase. In both the neutron-capture and isomeric-change reactions the presence of products of higher boiling point than CCl_3Br indicates the mechanism of reaction to be more complex than the removal of a single chlorine atom from carbon tetrachloride.

With bromine and tetrachloroethylene reactions in the gas phase, results indicate that probably no reaction takes place following neutron capture, but appreciable reaction follows isomeric transition of the bromine. In the liquid phase the probability of a bromine atom forming a bromo-organic compound following isomeric transsition is much greater than either the probability that it will do so as a result of neutron capture or the probability of its reaction with carbon tetrachloride.

The different probabilities of reaction following the two types of activation are discussed. The Franck and Rabinowitsch " cage " hypothesis (*Trans. Faraday Soc.*, 1934, **30**, 120) is supported by the difference in probability observed between reactions in liquid and gas phases.

E. H. W.

868. Hydrogen Fluoride as a Condensing Reagent. XVI. Reactions of Carbon Monoxide. J. H. Simons and A. C. Werner. *J. Amer. chem. Soc.*, 1942, **64**, 1356–1357.—Conditions are described by which carbon monoxide reacts in the presence of hydrogen fluoride with *iso*propyl chloride or *n*-propyl alcohol, but not *iso*propyl alcohol, giving *iso*butyric acid. In the absence of either water or methanol, *iso*propyl chloride did not yield the acid. The results are discussed and a mechanism for the reactions is proposed.

E. H. W.

869. Higher Hydrocarbons. I. Seven Alkyl-Substituted Docosanes. F. C. Whitmore, L. H. Sutherland, and J. N. Cosby. *J. Amer. chem. Soc.*, 1942, **64**, 1360–1364.—The syntheses of 11-*n*-butyl-, 9-*n*-butyl-, 7-*n*-butyl-, 5-*n*-butyl-, 7-*n*-hexyl, 9-*n*-octyl-, and 11-*n*-decyldocosanes are described. M.pt., b.pt. at 1·0 mm., n_D^{20}, d_4^{20}, molecular refraction, and viscosity at 20° C. are reported for each hydrocarbon, together with yields and properties for seventeen intermediates. Special emphasis is laid on the need for obtaining pure compounds, and the general problem of purity is discussed.

E. H. W.

870. Heats of Catalytic Hydrogenation of Solution. I. Apparatus, Technique, and the Heats of Hydrogenation of Certain Pairs of Stereoisomers. R. B. Williams. *J. Amer. chem. Soc.*, 1942, **64**, 1395–1404.—Measurement of the heats of catalytic hydrogenation in solution at room temperature are reported. The catalysts used were $PtO_2.H_2O$ or PdO, glacial acetic acid was the solvent. The apparatus and technique employed are described. To check the accuracy of the results, the heat of hydrogenation of *n*-heptane-1 in the gas phase at 355° K. was derived from the figure obtained at 302° K.

in glacial acetic acid solution, Kistiakowsky's figure obtained directly in the gas phase was in excellent agreement. Heats of catalytic hydrogenation in solution of the following substances are reported: 1 : 4-dihydronaphthalene, 1 : 2-dihydronaphthalene methyl *cis*-cinnamate, methyl *trans*-cinnamate, *i*-stilbene, stilbene, diethyl maleate, diethyl fumarate, 1 : 4-diphenylbutadiene. The results show agreement with the rules put forward by Kistiakowsky for the effect of substituents on the heat of hydrogenation of the ethylenic double bond. Values for the increase in stability due to conjugation of certain of the compounds are given, and the heats of isomerization of the pairs of stereoisomers are considered. The heat of complete hydrogenation of 1 : 2-dihydronaphthalene is shown to be greater than that for indene (the corresponding 5-membered ring compound). This result also agrees with previous reports by Kistiakowsky and co-workers on similar pairs of compounds. E. H. W.

871. Studies in Gaseous Hydrogenation and Polymerization Reactions. H. B. Burnham and R. N. Pease. *J. Amer. chem. Soc.*, 1942, **64**, 1404–1410.—Small initial additions of nitric oxide are shown to inhibit the polymerization of ethylene and acetylene, as well as the hydrogenation of ethylene. A chain mechanism is proposed for these reactions, and it is also suggested that the nitric oxide acts by combining with the free radicals or atoms, and thus effectively prevents their further participation in the chain reaction. Nitric oxide did not inhibit either the hydrogenation or polymerization of propylene; instead, a slight acceleration of the reactions was observed. This catalytic effect of nitric oxide neither favours nor denies the possibility of a chain mechanism in the propylene reactions studied. E. H. W.

872. The Mechanism of the Catalytic Reduction of some Carbonyl Compounds. L. C. Anderson and N. W. MacNaughton. *J. Amer. chem. Soc.*, 1942, **64**, 1456–1459.—A mixture of hydrogen (80 parts) and deuterium (20 parts) has been used in the catalytic reduction of *n*-butyraldehyde, acetaldehyde, acetone, diethyl ketone, and methyl ethyl ketone. The mechanisms of the reactions were studied by examination of the Raman spectra of the reduction products, these latter were oxidized, and the Raman spectra of the products determined.

In the presence of nickel, platinum, and copper chromite, reduction occurred at low temperatures through addition of hydrogen to the carbonyl group. At elevated temperatures, acetone and butyraldehyde were reduced to a considerable extent through the addition of hydrogen to the carbon–carbon double bond of the enol form.

It has been shown that in the presence of Raney nickel there was preferential addition of the HD molecule to the carbonyl group, forming CD and OH bonds. With *iso*propyl and *n*-butyl alcohols in the presence of nickel at 25° C. or platinum up to 250° C. deuterium was exchanged for the hydroxyl hydrogen, but with nickel or copper chromite catalysts at 250° C. exchange took place on the hydrogen of both the carbinol carbon atom and that of the adjacent carbon atom. In the latter exchanges the results were taken as evidence that dehydrogenation, enolization, and hydrogenation reactions were all involved. E. H. W.

873. Catalytic Hydrogenation of Heptaldehyde in Vapour Phase. T. J. Suen and S. Fan. *J. Amer. chem. Soc.*, 1942, **64**, 1460–1462.—The experimental procedure and identification of products are reported for the hydrogenation of heptaldehyde in the vapour phase under atmospheric pressure in the presence of a nickel catalyst.

The main product was *n*-hexane, together with some *n*-heptyl alcohol. Carbon monoxide formed in the degradation reaction was partly reduced to methane.

E. H. W.

874. The Ultra-violet Absorption Spectra of Coronene. Note by J. W. Patterson. *J. Amer. chem. Soc.*, 1942, **64**, 1485–1486.—Coronene is the simplest hydrocarbon in which benzene rings completely surround a central aromatic nucleus. The position and intensities of the bands and the ultra-violet absorption spectra are recorded.

E. H. W.

875. The Electron Diffraction Investigation of Propargyl Chloride, Bromide, and Iodide. L. Pauling, W. Gordy, and J. H. Saylor. *J. Amer. chem. Soc.*, 1942, **64**, 1753–1756.—The interatomic distances of the propargyl halides have been determined from electron diffraction measurements. The distances calculated were (assuming $C \equiv C$, 1·20 Å.): C–C, 1·47 ± 0·02 Å.; C–Cl, 1·82 ± 0·02 Å; C–Br, 1·95 ± 0·02 Å.; C–I 2·13 ± 0·03 Å. and the angles C–C–Cl, 111 ± 2°, C–C–Br 112 ± 2°, C–C–I 111 ± 3°. As with methylacetylene (*J. Amer. chem. Soc.*, 1939, **61**, 927), the C–C distance is less than normal; but the carbon halogen bond distances are somewhat larger than usual. E. H. W.

876. The Reduction of Unsaturated Hydrocarbons at the Dropping Mercury Electrode. I. Phenyl-substituted Olefins and Acetylenes. H. A. Laitinen and S. Wawzonek. *J. Amer. chem. Soc.*, 1942, **64**, 1765–1768.—This paper presents a polarographic study of a series of phenyl-substituted olefins and acetylenes. A solution of 75% dioxane and 25% water was used with tetrabutylammonium iodide as supporting electrolyte. Substances investigated included stilbene, triphenylmethane, diphenylbutadiene heptyne-1, *o*-allylanisole, phenylacetylene, styrene, 1 : 1-diphenylethylene β-methylstyrene, tetraphenylethylene, and diphenylacetylene. Half-wave potentials and diffusion-current constants determined are tabulated. All the hydrocarbons investigated showed a well-defined reduction wave. The half-wave potentials were generally independent of pH. The diffusion current was proportional to the hydrocarbon concentration in every case, and the polarographic method was claimed to be useful for the detection and determination of these hydrocarbons in the absence of more readily reducible substances. Further uses for the method were also claimed. A mechanism of the reduction was proposed. The diffusion coefficients of the hydrocarbons have been calculated from diffusion-current data. E. H. W.

877. The Formation of *cyclo*Propanes from Monohalides. III. Action of Sodium Alkyls on Aliphatic Chlorides. Relation to the Wurtz Reaction. F. C. Whitmore and H. D. Zook. *J. Amer. chem. Soc.*, 1942, **64**, 1783–1785.—The reaction of sodium with excess mercury diethyl in *n*-pentane solution at 25° C. gave an 80% yield of sodium ethyl. To this reaction mixture *n*-hexylchloride was added at −10° C. to 0° C., giving a yield of 40% *n*-octane, 46% yield of 1-hexene, and 52% yield of ethane, together with a small amount (2%) of ethylene. An 88% yield of sodium *n*-propyl was obtained from sodium and excess mercury di-*n*-propyl in *n*-octane solution. The sodium *n*-propyl reacted with neopentyl chloride at 50–60° C., giving a 75% yield of 1 : 1-dimethyl*cyclo*propane, 4% yield of 2 : 2-dimethylhexane, and 70% yield of propane, together with 5% yield of propene, the latter probably coming from the sodium alkyl. The chief reaction is the sodium alkyl acting as a hydrocarbo base and splitting out hydrogen chloride from an alkyl chloride. The base strength of the sodium alkyl is seen from the fact that neopentyl chloride does not react with alcoholic potash in a sealed tube at 100° C. for 20 hrs. The possible relationship of these results to the mechanism of the Wurtz reaction is discussed. E. H. W.

878. Higher Hydrocarbons. II. Five 11-Substituted Heneicosanes. F. C. Whitmore, J. N. Cosby, W. S. Sloatman, and D. G. Clark. *J. Amer. chem. Soc.*, 1942, **64**, 1801–1803.—Continuing previous work which reported the preparation and properties of seven alkyl-substituted docosanes (*J. Amer. chem. Soc.*, 1942, **64**, 1360), the present paper describes the synthesis and properties of five heneicosanes with different type substituents in the 11-position. Keeping the paraffin chain constant and changing the type of substituent (as now reported) had a much greater influence on the properties than either moving a side-chain or altering the molecular weight.

Particular care was taken to obtain pure compounds. In the compounds prepared the substituents were: *n*-amyl-, (3-pentyl)-, *cyclo*pentyl-, phenyl-, and *cyclo*hexyl-, in addition 11-phenyl-10-heneicosene was prepared. The constants given are m.pt., b.pt. (at 1·0 mm.), n_D^{20}, d_4^{20}, molecular refraction, and viscosity at 20° C. in cps. E. H. W.

879. The Compressibility of Liquid *n*-Octane. W. A. Felsing and G. M. Watson. *J. Amer. chem. Soc.*, 1942, **64**, 1822–1823.—The compressibility of liquid *n*-octane has been determined between 100° C. and 275° C. in 25° steps, and for pressures ranging from 5 to 300 atmospheres.

The specific volumes as functions of pressure are given, together with the specific volumes of liquid *n*-octane in contact with its vapour over the same range of temperature as the compressibilities. E. H. W.

880. The Dissociation of Hexa-arylethanes. XII. The Effect of Naphthyl and Biphenyl Groups. C. S. Marvel, J. W. Shackleton, C. M. Himel, and J. Whitson. *J. Amer. chem. Soc.*, 1942, **64**, 1824–1825.—Measurement by the magnetic susceptibility method of several hexaphenylethanes combining *a*-naphthyl, *β*-naphthyl, and *p*-biphenyl radicals is reported. The dissociations were all calculated at 0·1 molar concentrations by the mass law. The results obtained are lower than the reports in the older literature. *a*-Naphthyl groups caused a much higher dissociation than *β*-naphthyl groups, showing again the importance of the steric factor. E. H. W.

881. Tri-*o*-tolylmethane. P. D. Bartlett and J. E. Jones. *J. Amer. chem. Soc.*, 1942, **64**, 1837–1842.—A preparation of tri-*o*-tolylmethane is described. With phenyl*iso*propyl potassium the central metalation product potassium tri-*o*-tolylmethide was not formed, but instead, a tripotassium derivative which, by carbonation, forms the potassium salt of triphenylmethane 2 : 2′ : 2″-triacetic acid. This is in contrast to the behaviour of the related compounds, phenyldi-*o*-, diphenyl-*o*-, and tri-*p*-tolylmethane, which under the same conditions all yield monopotassium derivatives that form triarylacetic acids by carbonation. Various explanations for the relative inertness of the central carbon atom of tri-*o*-tolylmethane are discussed. E. H. W.

882. The Ternary Systems Involving *cyclo*Hexane, Water, and *iso*Propyl and Normal Propyl Alcohols. E. R. Washburn, C. E. Brockway, C. L. Graham, and P. Deming. *J. Amer. chem. Soc.*, 1942, **64**, 1886–1888.—Tabulated and graphical results are presented for the solubility relationships at 25° C. of the ternary systems containing water, *cyclo*hexane, and *iso*propyl alcohol, and at 25° C. and 35° C. for the ternary system containing water, *cyclo*hexane, and *n*-propyl alcohol. E. H. W.

883. The Viscosity of *cis*- and *trans*-Decahydronaphthalene. W. F. Seyer and J. D. Leslie. *J. Amer. chem. Soc.*, 1942, **64**, 1912–1915.—A detailed description is given of the determinations of the viscosities in centipoises of *cis*- and *trans*-decahydronaphthalene at 10° intervals from $-30°$ C. to 180° C. The viscometers were modifications of the Ostwald type, made in accordance with British Standards Specification No. 188–1937, and were calibrated with pure water. Curves for log η against $\frac{1}{T}$, although not linear, were smooth, but with the *cis*-isomer a deviation began at 110° C. Physical constants for *cis*- and *trans*-isomers of several other hydrocarbons are given, and in each case the *cis*-isomer has a higher boiling point, specific gravity, viscosity, and E_{vis} (the average molar activation energy for viscous flow).

A suggestion is made to explain the high values of η and E_{vis} of decahydronaphthalene and the effect of *cis*- and *trans*-isomerism on these. E. H. W.

884. The Hydration of *iso*Butene in Dilute Nitric Acid. G. R. Lucas and L. P. Hammett. *J. Amer. chem. Soc.*, 1942, **64**, 1938–1940.—The results of an investigation of the reaction between *t.*-butyl chloride and mercuric nitrate in various dioxane–water mixtures are given. In a semi-quantitative study of the hydration of *iso*butene in dilute nitric acid it was shown that the rate of disappearance of *iso*butene decreased rapidly when increasing proportions of dioxane were present. The results indicated that *t.*-butyl nitrate was not an intermediate in this reaction. Reasons for the increase in the rate of hydration on addition of nitrate ions are discussed. E. H. W.

885. Identification of Alcohols and Alkyl Hydrogen Sulphates with *S*-Benzylthiuronium Chloride. Note by R. S. Bair and C. M. Suter. *J. Amer. chem. Soc.*, 1942, **64**, 1978.—*S*-Benzylthiuronium chloride, produced by the action of benzyl chloride with urea, is shown to be a useful reagent for preparation of derivatives of alcohols and alkyl hydrogen sulphates. Alcohols are converted first into alkyl hydrogen sulphates by warming in dioxane solution with chlorosulphonic acid. Melting points and a description of the preparation of a number of derivatives are given. E. H. W.

886. The Dehydration of 1 : 5-Hexadiene-3-ol to 1 : 3 : 5-Hexatriene and 1 : 3-*cyclo*Hexadiene. Note by L. W. Butz. *J. Amer. chem. Soc.*, 1942, **64**, 1978–1979.—

The presence of 1 : 3-*cyclo*hexadiene in the hydrocarbons obtained by dehydrating 1 : 5-hexadiene-3-ol is confirmed, and reasons for its presence are discussed.
E. H. W.

887. The Dipole Moments of *cyclo*Hexanol and *cyclo*Hexanone in Dioxane. Note by I. F. Halverstadt and W. D. Kumler. *J. Amer. chem. Soc.*, 1942, **64**, 1982.—Measurements of the dipole moments of *cyclo*hexanol and *cyclo*hexanone in dioxane solution at 25° C. Evidence from the results showed that the compounds were not associated in dioxane solution. E. H. W.

888. The Ignition of Methane by Hot Wires. W. Davies. *Fuel*, 1943, **22**, 72.—Methane and air in explosive mixtures cannot be ignited by direct transmission of heat from a thin gold or platinum wire. Ignition occurs when the wire fuses, and it is then caused by the arc, and not by the heat of the wire. The m.pt. of platinum is 750° C. higher than that of gold, but ignition occurs more readily when the gold wire fuses. This is due to the catalytic action of the platinum wire, which renders the gas in the neighbourhood of the wire non-inflammable prior to the attainment of the fusion point. A contributory factor is the higher current flowing in a gold wire, diameter for diameter, which is required to cause fusion compared with a platinum wire. The breaking of this higher current causes a more powerful arc. J. W. H.

889.* Thermodynamics of the Liquid State. K. M. Watson. *Industr. Engng Chem.*, 1943, **35** (4), 398.—By means of an application of the theorem of corresponding states it is shown that it is possible to calculate, from a knowledge of the b.pt., critical temperature, critical pressure, and the liquid density at some one temperature, the following thermodynamic properties of liquids : thermal expansion and compressibility, pressure correction to enthalpy and entropy, pressure correction to heat capacity at constant pressure, latent heat, difference in heat capacity between a saturated liquid and an ideal gas, and the difference in heat capacity between a saturated liquid and heat capacity at constant pressure. Calculations of this type, like all applications of the theorem of corresponding states, do not give a rigorously correct answer, but the information obtained is usually sufficiently accurate for process design problems and is of great value in the correlation of fragmentary experimental data. J. W. H.

890.* Effect of Column Hold-up on Batch Rectification. E. Edgeworth-Johnstone. *Industr. Engng Chem.*, 1943, **35** (4), 407.—Previous workers have given methods of calculating the effect of column hold-up on the degree of separation at constant reflux. To conserve heat and time, it is common practice to start a distillation at a low reflux ratio and to increase it progressively as the cutting point is reached to maintain constant product composition. Equations are given which enable the effect of hold-up under the foregoing conditions to be calculated precisely for binary mixtures and approximately for complex mixtures. Examples are worked out illustrating the solution of the equations given for five-component mixtures. J. W. H.

891.* Effect of Temperature on Liquid–Liquid Equilibrium. S. W. Briggs and E. W. Comings. *Industr. Engng Chem.*, 1943, **35** (4), 411.—The experimental technique employed for the determination of the phase diagrams of the systems benzene–acetone–water and docosane–1 : 6-diphenylhexane–furfural is described. The equilibrium diagrams at a series of temperatures are given, and the values of these data in computing continuous extraction conditions with and without a temperature gradient are discussed. J. W. H.

892.* Design Calculations for Plate Columns. E. M. Baker and R. A. Lindsay. *Industr. Engng Chem.*, 1943, **35** (4), 418.—The application of the McCabe and Thiele method for the solution of a theoretical plate problem necessitates an assumption of constant molal overflow. This paper presents a method, based on enthalpy, for the calculation of theoretical plates when the molal overflow is not constant. The cases dealt with are : separation of one feed with no entrainment and separation of one feed with entrainment. Each of the cases is illustrated by an example. J. W. H.

893.* Correlation of Physical Properties of Paraffin Hydrocarbons. A. W. Francis. *Industr. Engng Chem.*, 1943, **35** (4), 442.—The boiling points of all the possible octanes (17), nonanes (34), decanes (74), and undecanes (159) have been calculated from the same properties of the next lower paraffins (precursors). The basis of the method used is the effect of the introduction of a methyl group in one of twenty-two possible ways. For each of these ways there is an increment in the physical property which is a simple ratio of the increment which is realized on the addition of a methyl group to the straight-chain hydrocarbon precursor. Good agreement is obtained between separate calculations of the same physical property by introducing the methyl group in a different manner. Where available it is shown that the calculated values are in agreement with those obtained by experiment, although in some cases there is strong evidence that a revision of the experimentally determined values may be required. Paraffin isomers with two branches on non-adjacent carbon atoms have almost identical boiling points. J. W. H.

894.* Electron Microscopy in Chemistry. Vladmir K. Zworykin. *Industr. Engng Chem.*, 1943, **35** (4), 450.—The applications of electron microscopy to chemistry are discussed and illustrated by micrographs of various materials, including carbon black, polyvinyl chloride, and polystyrene. Descriptions are given of the various techniques employed, such as stereomicrophotography, diffraction patterns, surface replicas, and scanning. J. W. H.

895.* Ternary Liquid and Binary Vapor-Liquid Systems. C. E. Dryden *Industr. Engng Chem.*, 1943, **35** (4), 492.—A method of correlating the distribution of the components in a ternary liquid system is described, and a method of applying this data to successive theoretical stages in an extraction system is given. Ten different systems are shown to conform to the hyperbolic equation used for making the correlation, and among these the ternary system methyl*cyclo*hexane–aniline–*n*-heptane occurs. J. W. H.

896.* Graphical Interconversions for Multicomponent Systems. J. D. Leslie. *Industr. Engng Chem.*, 1943, **35** (4), 495.—The method of Sun and Silverman for making interconversions of weight, volume, and molar compositions has been extended to multiple systems. J. W. H.

897.* Interconversions of Polycomponent Compositions by Graphical Methods. K. H. Sun and A. Silverman. *Industr. Engng Chem.*, 1943, **35** (4), 497.—Simple graphical methods are described for the interconversion of weight, volume, and mole fraction for polycomponent systems. J. W. H.

898. The Viscosity of Dilute Solutions of Long-Chain Molecules. M. L. Huggins. *J. appl. Phys.*, 1943, **14** (5), 246.—The effect of the solvent on the viscosity of dilute solutions of long-chain molecules is treated mathematically. Experimental data are given for solutions of polybutene and polystyrene in a number of hydrocarbon and other solvents. From these data it is shown that the values of $\eta s_p/c$ for a solution of a given polymer are symbatic with the proportion of a poor solvent which must be added to cause precipitation. J. W. H.

899.* Prediction of Reaction Rates. F. Daniels. *Industr. Engng Chem.*, 1943, **35** (5), 504.—Examination of thirty unimolecular gas reactions shows that a simple Arrhenius equation can be applied. Empirical and theoretical rules for predicting reaction rates are examined and recommendations made. The practical application of reaction-rate equations is discussed. J. W. H.

900.* Organic Reactions. H. Eyring, H. M. Hulbart, and R. A. Harman. *Industr. Engng Chem.*, 1943, **35** (5), 511.—The basic theory of the thermodynamics of reaction rate are given, and the types of activated complex which govern the reaction rate are discussed. The theory of the following types of reaction are reviewed : intramolecular rearrangement, double bond reactions, and heterogeneous reactions. J. W. H.

901.* Principles of Reactor Design for Gas-Solid Interface Reactions. D. M. Hurt. *Industr. Engng Chem.*, 1943, **35** (5), 522.—A method of correlating the performance of small- and large-scale reactors in gas-solid interface reactions is given. This new method involves the concept of H.R.U. (height of overall reaction unit) and H.C.U. (height of a catalytic or surface reaction unit). These terms are used in conjunction with the conventional gas film H.T.U. as a measure of mass transfer rate. Experimental data are given correlating heat and mass transfer rates with the Reynolds' number. J. W. H.

902.* Solid Catalysts and Reaction Rates. O. A. Hougen and K. M. Watson. *Industr. Engng Chem.*, 1943, **35** (5), 529.—From the activated adsorption theory reaction-rate equations are developed for chemical reactions catalysed by solids. The derivation of the basic equation is given, and from this a simplified equation is derived for monomolecular surface reactions. Equations are also derived for bimolecular–monomolecular and bimolecular–bimolecular reactions. Quantitative expressions are proposed for the effects of adsorption, dissociation, catalyst activity, particle size, flow conditions, poisons, diluents, temperature, pressure, and concentration. Methods of integrating these equations for the design of commercial reactors are given. J. W. H.

903.* Conduction, Convection, and Heat Release in Catalytic Converters. R. H. Wilhelm, W. C. Johnson, and F. S. Acton. *Industr. Engng Chem.*, 1943, **35** (5), 562.—Solutions are presented for the thermal equations involving the rate of heat generation in cylindrical and slab-shaped catalyst beds, the rate of removal of heat by convection between solid and gas, and its removal by conduction through the catalyst and gas in a direction perpendicular to the direction of flow of the gas stream. To simplify the use of the equations, the functions are plotted in dimensionless form, and by the use of these graphs a practical problem is worked out. J. W. H.

904.* Thermodynamic Properties of Propane. W. N. Stearns and E. J. George. *Industr. Engng Chem.*, 1943, **35** (5), 602.—From the physical properties of propane determined by various workers, a wide-range temperature–entropy and Mollier diagram has been constructed. The method employed for correlating the various data is described. J. W. H.

905.* Composition of Vapours from Boiling Binary Solutions. D. Othmer. *Industr. Engng Chem.*, 1943, **35** (5), 614.—A detailed description is given of an all-glass apparatus for the determination of the vapour–liquid equilibria of binary mixtures at pressures from 1 mm. Hg to atmospheric pressure. Vapour–liquid equilibria data are given for twenty-six binary systems. These mixtures include data on the systems acetic acid–toluene, acetic acid–xylene, acetone-benzene, acetaldehyde-benzene and acetaldehyde-toluene. J. W. H.

906. The Fundamental Problem of the Theory of Viscous Fluids. H. Putman. *J. appl. Phys.*, May 1943, **14** (5), 244–245.—An hydrodynamic approach based on the Navier–Stokes equations, the equation of continuity, and the characteristic equation is suggested for the theory of viscous fluids. The viscosity is assumed constant. A. H. N.

907. Pressure-Temperature Relations of Petroleum Fractions. W. L. Nelson and W. Haltenberger, Jr. Part I. *Oil Gas J.*, 11.6.42, **41** (5), 38. Part II. *Ibid.*, 18.6.42, **41** (6), 40.—The purpose of the work was to provide data on pressure-temperature relations of moderately wide boiling-range petroleum fractions, and to relate their behaviour to that of narrow boiling-range fractions and pure normal paraffin hydrocarbons, whilst the experimental method adopted consisted of A.S.T.M. and Engler type distillations at different pressures varying from 25 to 760 mm. Hg. Data are presented graphically and in tabular form. The effect of vacuum is to displace the distillation curve vertically by a constant amount. Methods of correlating vapour pressure with temperature are discussed and vapour pressures calculated from the distillation data give approximately straight converging lines on a Cox chart. Change of pressure alters the boiling points of the petroleum fractions somewhat less than those of the pure paraffins, whilst lines of constant percentage distilled deviate slightly from those of the pure paraffins. The effect of temperature on the change of boiling point with pressure is less pronounced for petroleum fractions than for normal paraffins, the deviations tending to increase with increasing boiling range of the fraction and being greatest for the initial boiling points of low-boiling fractions and for the final boiling points of high-boiling fractions. It is concluded that the differences are not sufficient to affect refinery design computations to a practical extent, and hence the use of the vapour pressures of paraffin hydrocarbons for evaluating the effect of pressure on petroleum fractions need not in most instances be abandoned. J. C.

Analysis and Testing.

908. A New Recording Viscometer for Paint-Consistency Measurements. C. R. Wicker and J. A. Geddes. *A.S.T.M. Bull.*, January 1943, **120**, 11. *Paper Presented before A.S.T.M.*—A new recording viscometer, combining the principles of the modified stormer and the McMichael instruments, is described. A cylindrical container is rotated at constant speed, the liquid within imparting torque to a paddle connected with a spring. A lever arm records the consistency upon a moving chart. Speed of rotation can be varied from 30 to 285 r.p.m. The instrument has been calibrated in grams/200 r.p.m. on the modified stormer, in Krebs units, and in absolute units for viscous liquids. Calibrations are essentially straight-line functions. Using one spring only, the viscometer covers a range of 100–850 stormer grams/200 r.p.m., 60–135 Krebs units, or 5–45 poises, which includes the practical range of paint consistencies. Springs of different characteristics can be used to extend the range.

Stress–strain curves obtained on this instrument are similar to comparable data from modified stormer viscometer data. Unlike the stormer, however, the recording viscometer can be used to obtain a continuous record of consistency. It is therefore possible not only to measure thixotropic and rheopectic paints, but also to follow the thickening of water-sensitive systems, effect of bodying agents, and similar phenomena of interest to the paint chemist. Less skill and experience are required to operate the recording viscometer, and a series of determinations can be made somewhat more rapidly than on the modified stormer. The new viscometer therefore appears suited for control work as well as research consistency measurements. A. H. N.

909.* Equipment for Viscosity Measurement. Part 2. Timing Devices. L. A. Steiner. *Petroleum*, May 1943, **6** (5), 72.—Three types of timing devices may be used for viscosity measurement: spring-driven stop-watches, mains-driven stop-clocks, and timing devices with constant-time base. The error curve of stop-watches is particularly disturbing in calibrations. Precision timing is extremely useful to manufacturers of viscometrical apparatus, for routine calibrations, and for the accurate determination of viscosity. Recent developments in radio technique have enabled the construction of precision-timing devices which are in several respects superior to other types and will find increasing application even when stop-watches are plentiful again. A single unit of this type easily replaces six stop-watches, and is, consequently, economical whenever the number of viscosity determinations is large. For occasional use stop-watches are to be preferred. The characteristics of each class are discussed in detail, sources of errors and methods of control being indicated. A. H. N.

910.* Equipment for Viscosity Measurement. Part 3. Constant-Temperature Baths. L. A. Steiner. *Petroleum*, June 1943, **6** (6), 88.—Temperature-control baths and systems—for viscometric studies—are discussed, with a brief historical sketch. Regulators and relays are studied in some detail. Heat transfer and temperature lag in viscometers are explained with some experimental determinations. A. H. N.

Lubricants and Lubrication.

911.* Deacidification of Transformer Oil by Activated Alumina. J. L. Ferns. *Petroleum*, March 1943, **6** (3), 34.—Results of preliminary experiments carried out by the author, using the percolation method only, are given and reference is made to data presented before the A.I.E.E. by J. E. Housley. Activated alumina sold for refining purposes consists of about 80% aluminium oxide and 20% of chemically combined water with but few traces of impurities. The method of manufacture in England differs from that employed in the U.S., but the English product is claimed to be superior for the purpose described. General characteristics are tabulated. In view of the affinity which activated alumina possesses for water, the material should be kept dry before use and the oil to be deacidified should be filtered before treatment. Reactivation with a loss of the order of 3% can be achieved by passing hot air through the used alumina in a suitable container, in order to start combustion of the oil content, and then maintaining the temperature of the alumina during the combustion process at 200–250° C. so as to retain the dehydrating properties. The reactivation takes about 3 hrs. and the material should be restored to its original whitish state. A reactivator constructed by the author is described and illustrated.

For the percolation process the popular grade of alumina is the 4/8 mesh, and as the material is free from dust, only a suitable retaining mesh is required. A reasonable depth of bed to avoid passage of liquid without contact with the medium is easily arranged, since, owing to its strength, the alumina will support a considerable weight on a grating, permitting columns of 6 ft. or more to be used if desired, provided the ratio of height to diameter is about 5/1. One of the advantages of activated aluminium is that its deacidifying properties are consistent and its effects are calculable in terms of acidity of the oil, time, and quantity of material. A table shows the approximate weight of activated alumina required to effect a specified improvement in acid value of oil under treatment—*e.g.*, oil having an initial organic acidity equivalent to 2 mgms. KOH/gm. requires treatment with 14 lb. activated alumina per 100 lb. of oil in order to reduce acid value to 0·05 mgm. KOH/gm.

Three methods investigated are : (1) Connecting a container charged with alumina to the transformer and relying upon thermal circulation to create a flow of oil through the container. This method is of advantage when it is not desirable to take the transformer off load or where a preventive treatment is envisaged, for example in the case of a transformer known to suffer from a high-acidification rate. The size of container used will determine the frequency with which the alumina must be changed. (2) Where it is possible to change the oil in the transformer and wash down cores and tubes, it is probably better to treat the oil in a special tank fitted with gauze trays filled with alumina and with arrangements for circulating the oil through the trays. From experiments conducted in a 200-gal. tank it is estimated that a 600-gal. tank charged with 1200 lb. of alumina would give a reasonably quick treatment. Colour is a fair indication of the condition of the oil. (3) Suitable containers filled with alumina may be placed inside the transformer in a safe position near the top of the oil.

Consideration is given to the application of activated alumina to the treatment of switch oils, oils used in oil-filled bushings, turbine oils, etc. R. A. E.

912. Emulsion Lubricants. Anon. *Chem. Tr. J.*, 12.3.43, 251.—This is a summary of a paper in *Oel und Kohle*, No. 9, 1942, and describes the development of emulsion lubricants by a Hamburg Company.

The mineral oil as sold for this purpose apparently contains an emulsifying agent. The user is then instructed how to prepare the emulsion.

It is recommended that the water should not be too hard and should be maintained at 20° C. Equal volumes of water and oil are advised, the water being added to the oil with continuous agitation by hand for small-scale work or a homogenizer of the Hurrell type for large quantities.

The emulsions are of the water-in-oil type and show thixotropic properties. They are stable at temperatures down to −30° C. An example is given of an emulsion suitable for lubricating the cylinders of large gas-engines and compressors.

Other uses for these lubricants are stated to be for shafting bearings, reciprocal compressors and plant driven by compressed air.

The saving of oil in practice is not quite 50%, since about 15% to 20% more emulsion is used than is the case with the non-emulsified oil. D. L. S.

913. Vegetable Oils as Engine Lubricants. Anon. *Gas Oil Pwr*, April 1943, **38** (451), 81. —This paper summarizes results obtained from experiments carried out under the auspices of the Indian Scientific and Industrial Research Dept. and given in detail in two bulletins, Nos. 18 and 20.

Vegetable oils in general possess better oiliness properties and lower coefficients of friction than mineral oils. They also compare favourably with mineral oils as regards viscosity index.

On the other hand, vegetable oils decompose at lower temperatures and are less stable to oxidation. Oxidation tests were carried out on a number of vegetable oils in the presence of steel balls. Polymerization was found to occur more easily than with petroleum oils, even when stabilizers were added. The development of acidity was more pronounced, and higher Conradson Carbon figures were obtained. Some stabilizers were found to be effective for castor, rape, and groundnut oils, but few were effective for cotton-seed oil. In general these stabilizers were compounds containing more than one benzene nucleus, and amongst these phenols and aromatic amino-compounds were effective.

However, neither the phenolic hydroxyl nor the amino-groups were themselves wholly responsible for these inhibiting properties, since compounds having three phenolic hydroxyl groups such as pyrogallol and *p*-phenylenediamine did not prove to be the best stabilizers. D. L. S.

914. Studies in Lubrication. Part 9. Temperature Behaviour of Journal-Bearing Systems. M. Muskat and F. Morgan. *J. appl. Phys.*, May 1943, **14** (5), 234—. Transient bearing temperature and friction data have been obtained for a journal-bearing system operating under thick-film conditions. The journal speed was varied from 1·5 to 11·0 r.p.s., and tests were made with five different lubricants. Equilibrium values of temperature and friction were determined by exponential extrapolation of data taken over time intervals of 3–6 hrs. By inversion of the Petroff formula, average film temperatures were calculated from the friction data. These were in all cases greater than the directly measured bearing temperatures, although the excess was in general less than 10° F. The equilibrium temperature data for the various lubricants and speeds were correlated on the basis of heat-balance considerations by the formula :

$$\mu N^2 = \text{const}\ (T - T_a)^{1\cdot35},$$

the film viscosity μ and temperature T referring to equilibrium conditions, T_a denoting the ambient temperature, and N the journal speed. This relation permits the calculation of the equilibrium conditions for a journal-bearing system of the type used here for any lubricant and journal speed. The asymptotic rate of approach to equilibrium was also quantitatively correlated to the final equilibrium conditions. For Gulflube 10 the equilibrium frictional force was found to increase monotonically with the journal speed, the rate of increase quickly tapering off for speeds greater than 4 r.p.s. Its value at 11 r.p.s. is only 0·14 of that to be expected if there were no fall in film viscosity. For Gulflube 30 the friction-force curve rises to a maximum at 3 r.p.s. and then falls slowly for greater speeds. The value at 11 r.p.s. is here only 0·04 of that for a constant-film viscosity system. A. H. N.

915. The Fundamental Problem of the Theory of Viscous Fluids. H. Putman. *J. app. Phys.*, 1943, **14** (5), 244.—The proof of a theorem is given from which, if the distribution of $\bar{\gamma}$, p, and ρ of all viscous particles at time t is known, the distribution at any subsequent time can be calculated. From this, if dw/dt is known, then $d(\Delta - \gamma)/dt$ can be calculated. J. W. H.

916.* Catalysis in the Oxidation of Lubricating Oil. R. G. Larsen and F. A. Armfield. *Industr. Engng Chem.*, 1943, **35** (5), 581.—A detailed study has been made of the catalytic effect of metallic iron, copper, and lead, and the naphthenate of these metals on three lubricating oils representative of Pennsylvanian, Midcontinent, and Californian stocks. It is shown that the variation in susceptibility with each of these materials is so great that no specified catalyst can be used in laboratory oxidation tests unless correspondence with engines is first well established. The catalytic effect of engines on oils was also studied by examining the oxidation characteristics of crankcase oils after various periods of service. It was found that these oils were very susceptible to oxidation, and this was found to be due to " crankcase catalysts," which, on removal by centrifuging, decreased the oxidation susceptibility, and when added to new oils increased the susceptibility. It is shown that this catalytic activity resides in the metallic components, particularly the halides of iron. J. W. H.

Asphalt and Bitumen.

917.* Measurement of the "Firmness" of Asphaltic Bitumens. D. C. Broome. *Petroleum*, July 1942, **5** (7), 122.—Until comparatively recently pitches were tested in some cases by "chewing" or twisting tests which, when carried out by experienced men, gave astonishingly accurate results. However, the personal factor has now been eliminated as far as possible from "firmness" tests on bituminous materials.

It has been suggested that for materials with properties intermediate between those of a true liquid and a Hookean solid firmness can be expressed by the equation: $\psi = S\sigma^{-1}t^k$, where σ is the strain produced by a shearing stress S, t is time, and k varies from zero for an elastic solid to 1 for a true liquid.

The author has found that the values calculated by this equation from experimental test results depend considerably on the conditions of test, and that "firmness" cannot yet be fully expressed in terms of fundamental units.

The A.S.T.M. penetration test appears to be the most valuable routine control test available, and tests with varying loads or temperatures are sometimes useful. However, there may be quite large differences in the effective "firmness" of bitumens which are not reflected in the penetration figures.

If the bitumen is at all plastic some idea of this plasticity may be gathered from the difference between its determined absolute viscosity and the absolute viscosity calculated from the penetration as indicated by Saal and Koens.

It has also been noticed that if a constant stress be applied to a bitumen, the rate of shear does not always remain constant over a period of time. It may increase due to thixotropy or decrease due to work hardening.

Another factor influencing "firmness" tests is the thermal history of the sample.

Allied to the problem of deformation under stress is the question of recovery after removal of stress. The recovery/time curve generally conforms approximately to the equation: $\sigma = aS(1 - e^{-b_2 t/a}) + b_1 St$, where a, b_1 and b_2 are constants and the other symbols have the significance indicated above.

Resistance of the material to tensile stresses is usually measured by ductility at 25° C., but the value of this test would be increased if temperature and rate of strain were varied.

Many other methods of measuring "firmness" not discussed in the paper may be available. D. L. S.

918.* Asphalt–Polybutene Paints. H. C. Evans, D. W. Young, and R. L. Holmes. *Industr. Engng Chem.*, 1943, **35** (4), 481.—The results of weathering tests on a large number of experimental asphalt–polybutene cut-backs, with and without fillers, show that polybutene considerably improved the water resistance. Less than 10% of polybutene is required to produce this effect, the quantity depending on the type and origin of the asphalt. J. W. H.

Special Products.

919. Preparation of 1·3 Butadiene from Petroleum and its Fractions. Translated from the Russian by J. G. Tolpin. Part I. *Oil Gas J.*, 11.2.43, **41** (40), 61.—Results are given of a detailed investigation carried out in the U.S.S.R. on crude oils of different types and their fractions from the point of view of preparation of dienes therefrom. The two main purposes of the research were: (1) to determine conditions for optimum yields of 1 : 3-butadiene from various oil fractions, and (2) to develop a sufficiently precise method of determination of 1 : 3-butadiene formed in the process of pyrolysis.

Baku crude oils, mazut, gasoline Grade 2, four close-cut fractions of Baku gasoline rich in naphthenes, and kerosine and solar oil of Caucasian origin were examined. The apparatus employed is illustrated, and is based on the application of a short heating period and rapid cooling of the reaction products, on account of the known instability of 1 : 3-butadiene at high temperatures. Neither reduction of pressure to any considerable extent nor dilution with inert gas was employed, although these factors are known to improve yields of butadiene. In determining the most favourable conditions for processing, only temperature and rate of flow were varied. The temperature survey, made at an arbitrary feed rate, showed that yields of butadiene from the gasolines were more susceptible to variation in temperature than yields from the heavier products and crudes. Optimum temperatures ranged from 715° C. for mazut to 750–755° C. for gasoline and its fractions. It was also established that optimum yields from gasoline and its fractions were much greater than from the heavier products.

The effect on yield of varying the rate of flow was then determined for each product at its determined optimum-yield temperature. Again variations were greatest with gasoline; velocities for optimum yields were within the range of 0·4–0·5 mls./min./sq. cm. cross-section of the furnace tube for all products examined.

Under the most suitable conditions of temperature and feed rate the maximum yields of butadiene obtained from the various fractions examined were: mazut 2·5%, solar oil 4%, kerosine 5·5%, gasoline 11%. The 101–103° C. cut from gasoline (largely methyl*cyclo*hexane) gave yields comparable with those from Grade 2 gasoline, but yields from the other three cuts were lower.

The method used for determination of butadiene produced is based on the fact that the hydrocarbon forms only crystalline tetrabromides, one form having a m.pt. of 118° and the other 39° C., whereas with other decomposition products crystalline bromides are either unknown or their formation in considerable quantity is improbable. Decomposition gases after cooling to 0° C. were passed through two brominating vessels in series, before passing to the gasometer. Care was taken to air-blow the apparatus and tar produced in order to displace or extract all butadienes. The liquid mixture of bromides obtained was washed with alkali and water distilled on a water-bath at 10–20 mm. pressure, to remove the bromides boiling under these conditions, and leave a cake of crude tetrabromide. These bromides were decomposed with zinc shavings and alcohol and the liberated gases analysed for olefines and di-olefines by the method of Dobryanskii. Since the regeneration efficiency of pure 1 : 3-butadiene under similar conditions was found by experiment to be 90–95%, a correction factor was applied to the butadiene determined in the regenerated gas, although it is admitted that a certain amount of di-olefines and traces of acetylene are recorded as butadiene by the method employed.

Part II. *Oil Gas J.*, 25.2.43, **41** (42), 76.—More complete details are given of the apparatus employed for the experiments, and analyses of the feed stocks utilized are provided. Results of a series of experiments carried out on each feed stock are presented in a series of tables showing decomposition temperature, rate of flow of oil in mls./min./sq. cm. cross-section of furnace tube, amount of oil decomposed, quantity and melting points of bromides obtained, and yield of 1 : 3-butadiene expressed as percentages of intake. R. A. E.

920.* Vinylidene Chloride Polymers. R. C. Reinhardt. *Industr. Engng Chem.*, 1943, **35** (4), 422.—The polymer reactions, chemical structure, physical properties, and methods of use in fabrication processes are discussed. J. W. H.

921.* Brittle Temperature of Rubber under Variable Stress. A. R. Kemp, F. S. Malm, and G. G. Winspear. *Industr. Engng Chem.*, 1943, **35** (4), 488.—An apparatus and experimental technique are described for determining the point at which rubber and similar materials fracture under variable bending stress when applied at temperatures down to −78° C. Experimental data are given for a large number of different rubber compounds. J. W. H.

922. The Mode of Action of Pyrethrum on the Cockroach. D. N. Roy, S. M. Ghosh, and R. N. Chopra. *Ann. Applied Biology*, May 1943, **30** (1), 42.—The first effect of pyrethrum on cockroaches is to cause intense irritation, followed by destruction of the nerve ganglia resulting in muscular paralysis, followed by deaith if the dose is heavy enough. Pyrethrin, the active principle, is insoluble in water but soluble in the body-fluid of the cockroach, so that the final result is the same, whether introduced into the body-cavity in the dry form or as a solution in kerosine. When introduced into the tracheal trunks as a solution, it is considered to diffuse through the tracheal wall into the body-cavity, and hence to the nerve ganglia, and when introduced as a powder it must be dissolved by the tracheal fluid which is concluded to be analogous to the body-fluid, since it has been shown by experiments with chalk, etc., that the action is not one of mechanical blocking. It has also been shown that pyrethrum when swallowed by the cockroach with its food, in a dry or a fluid state, has no effect. C. L. G.

923. A Versatile Oil-Testing Cell of Novel Design. T. Hazes. *Rev. Sci. Inst.*, 1943, **14** (5), 141.—A description is given of a simple cell for the routine determination of the electrical properties of insulating oils. This cell is very easily constructed from readily available materials. J. W. H.

924. Floor Wax. Anon. *Soap*, June 1943, **19** (6), 113.—The tentative specifications and standard methods of testing of water emulsion floor waxes which have been adopted by the U.S. National Association of Insecticide and Disinfectant Manufacturers are quoted. C. L. G.

925. Insect Kill. The Action of Insecticides on Insect Tissue. A. Weed. *Soap*, June 1943, **19** (6), 117.—A brief review is given of experimental work carried out by various investigators on the manner in which insecticides affect insect tissues. Arsenical compounds, which act as stomach as well as contact poisons, have been noted to cause separation of epithelium and connective tissues in the intestines, disintegration or intensified division of red corpuscles, and reduced oxygen consumption. Their effectiveness is related to solubility in the digestive tract, the pH value of the digestive fluids, and the buffering power of the juices and gut contents. Fluorine compounds behave similarly, and also upset the calcium balance and interfere with the catalase and oxidase activities of insect tissue extract. Petroleum oils can cause death by (1) suffocation, by blocking of the respiratory system, (2) destruction of tissue following penetration, and (3) fumigant action. With scale insects the unsaturated compounds are toxic through (2) or (3). Volatile oils pass through the entire body-cavity of scale insects, dissolving the fat and even the entire cellular structure, whereas highly refined kerosine is frequently expelled and has little effect. Heavier refined oils remain in the trachea, causing suffocation, although, in view of the diffusion of oxygen and carbon dioxide through thin films of oil, the toxicity may be due to unsaturated compounds. Gasoline and kerosine vapours are absorbed by insects and slowly given off, toxicity being due to prevention of oxygen absorption by the tissues. It has been found that petroleum oils cause clumping of the chromatin in the nuclei, particularly in the central nervous system, of mosquitoes, this being considered a criterion of asphyxiation. With rotenone, no injury to nerve-tissue has been noted, death being considered due to respiratory failure, although desiccation and starvation are also probable factors. Thiocyanates in general kill insects through injury of nerve-tissue. Pyrethrum causes destruction of the cells of the central nervous system, followed by paralysis. *iso*Butyl undecyleneamide causes dissolution of the chromatin. Pyrin—a mixture of *iso*butyl undecyleneamide and pyrethrum—combines the effect of both constituents, but causes a greater breakdown of the interior ganglionic mass than does pyrethrum alone.

A detailed bibliography is given. C. L. G.

Economics and Statistics.

926. World Consumption of Petroleum and Its Substitutes During 1942. W. R. Garfias, R. V. Whetsel, and J. W. Ristori, *Petrol. Tech.*, May 1943, *A.I.M.M.E. Tech. Pub. No.* 1595, 1–3.—Since U.S.A. entered the war virtually all data and information necessary for compiling figures on world petroleum consumption have become unavailable. It is becoming clear that after the war the presentation of a comprehensive idea of the state of the petroleum industry will require the co-operation of statistical bureaux in countries outside U.S.A.

It has been possible to make a rough estimate of the world output of crude petroleum and petroleum substitutes for 1942, and the total is given as 2,208,000,000 brl., a decrease of 171,000,000 brl. below 1941. Crude production is believed to have fallen by about 200,000,000 brl., while the production of substitutes has risen by 28,500,000 brl. (nearly 20%). The U.S.A. crude output declined by about 19,000,000 brl., or under 2%; foreign production is estimated to have fallen by 180,000,000 brl., or more than 20%. Large decreases in output took place in Venezuela and Colombia due to lack of transport.

The 1942 oil output in Japan may have risen to 10,000,000 brl., and the Japanese production from captured fields may have been 23,000,000 brl., thus giving a total some 8,000,000 brl. greater than the peace-time requirements of Japan.

The Axis output in 1942 may have been 112,000,000 brl., 20% more than the 1941 figure. Germany may have produced 46,000,000 brl. of petroleum substitutes. The Axis consumption is estimated at roughly 13,000,000 brl./month during active military operations and 9,000,000 brl./month between campaigns. The increase in substitutes may indicate the ineffectiveness of aerial attacks on German synthetic plants or that the location of all these widely distributed plants is not known. G. D. H.

927. Capital Flow and Capital Formation in the Petroleum Industry, 1934–1941. J. W. Pogue and F. G. Coqueron. *Petrol. Tech.*, May 1943, *A.I.M.M.E. Tech. Pub. No.* 1597, 1–12.—Analysis of the financial data covering a representative group of thirty oil companies for a period of eight pre-war years, aside from constituting an economic and accounting record, leads to several broad conclusions: (1) The petroleum industry generated the capital necessary for its maintenance and expansion, thus constituting a self-reliant industry. (2) The net increase in debt was very modest and the existing ratio of debt to other forms of capital is conservative. (3) Investments in fixed capital assets increased in importance between 1934 and 1941, and current assets became less important in relationship to borrowed and invested capital. (4) Nearly two-thirds of the capital invested went into the producing branch of the industry, indicating the high cost of replacing and increasing crude-oil reserves. (5) The efficiency of capital utilization is indicated by the fact that the thirty oil companies under review increased their crude-oil production by 55% and their runs to stills by 52% between 1934 and 1941 as compared with a net expansion of 23% in gross fixed capital assets. (6) The gross investment in fixed capital assets of thirty oil companies on 31st Dec., 1941, was 10,173 million dollars, divided as follows: production 49·0%; transportation, 15·2%; refining, 18·7%; marketing 15·1%; and all other, 2·0%. (7) The flow of funds exhibited cyclical variations, expenditures for capital investments fluctuating with changes in the price of crude oil. (8) The return on invested capital for twenty-nine oil companies for eight years averaged 6·4% against 8·7% for a group of over 1100 manufacturing companies. (9) The consolidated statements here submitted point to an oil economy functioning soundly and effectively.

Data are presented in thirteen tables and five figures. G. D. H.

INSTITUTE NOTES.

SEPTEMBER, 1943.

HONOURS.

Lt.-Commander J. R. Smellie, R.N.V.R., has been awarded the Distinguished Service Cross for gallantry at sea and devotion to duty.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute. In accordance with the By-Laws, the proposals will not be considered until the lapse of at least one month after the publication of this *Journal*, during which time 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 the candidate.

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

The names of candidates' proposers and seconders are given in parentheses.

HOLMES, Harold Richard, Installation Supervisor, "Shell" Refining and Marketing Co., Ltd. (*G. Davidson ; E. Stokoe.*)

HUDSON, Cyril Henry, Sales Director, Sterns, Ltd. (*A. L. Read ; A. M. Nicholas.*)

JU, Ting Yih, Chemical Engineer, Universal Trading Corpn. (*Application for Transfer to Associate Member.*)

LINDSAY, James, Superintendent, Anglo-American Oil Co., Ltd. (*J. E. Jenkin ; F. Tipler.*)

LOWE, Robert, Assistant Regional Manager, Petroleum Board. (*V. M. Farrant ; E. J. Dunstan.*)

MAUCHAN, Alexander Callander, Chemist, Petroleum Board. (*C. Chilvers ; E. B. Evans.*)

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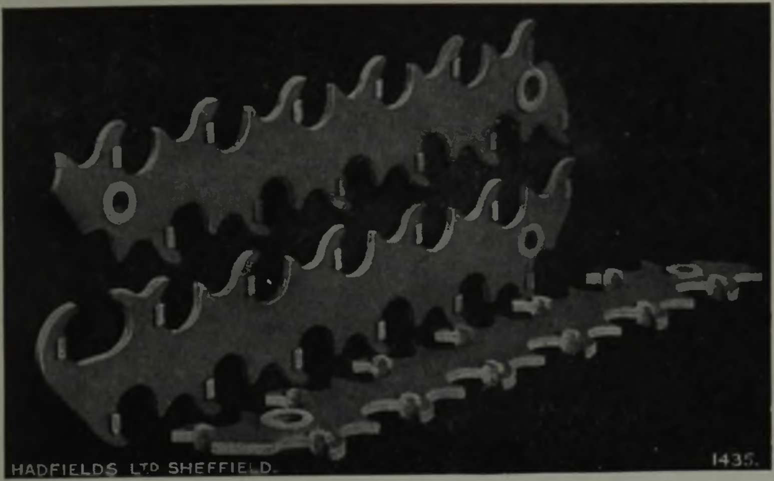
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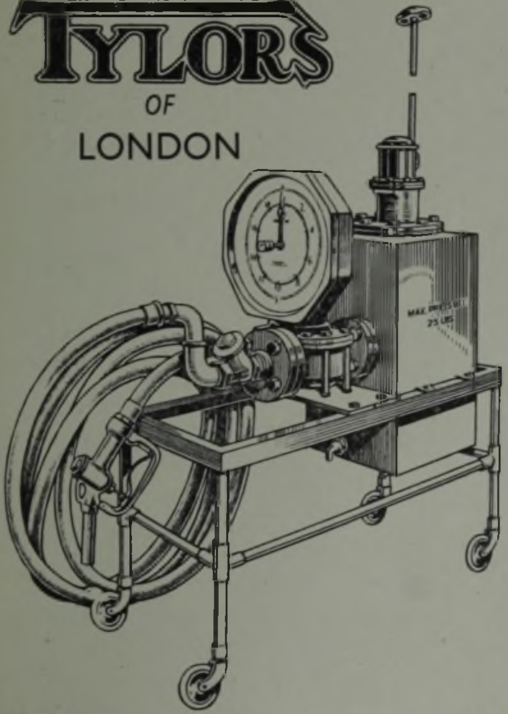
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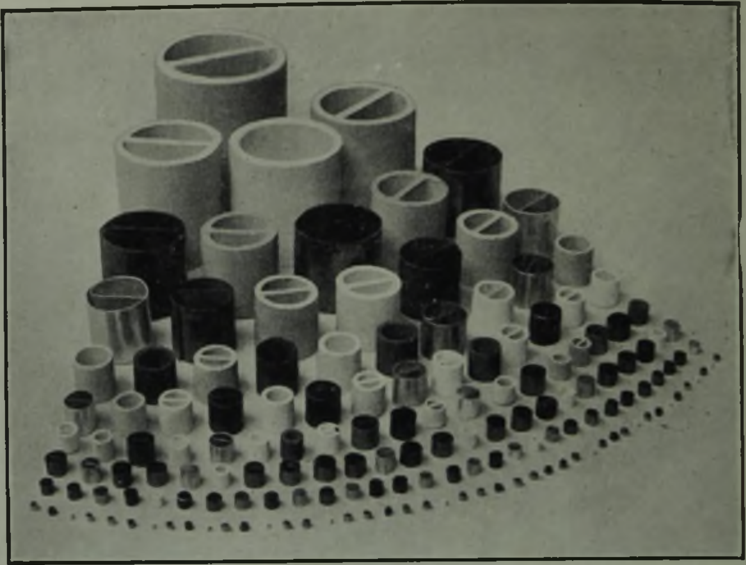

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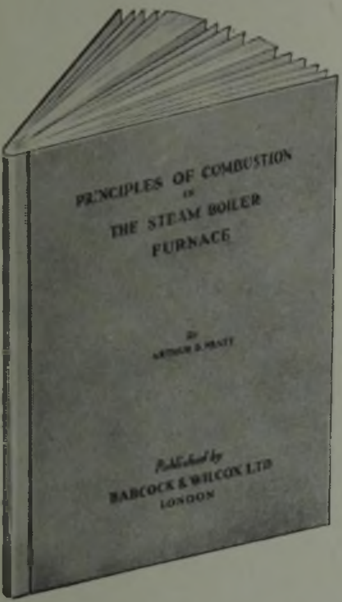
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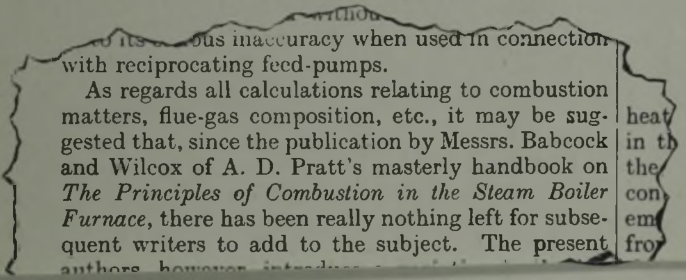

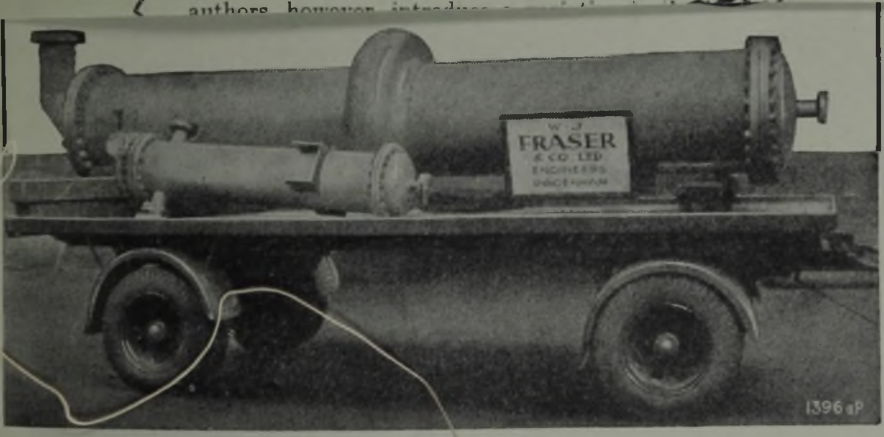
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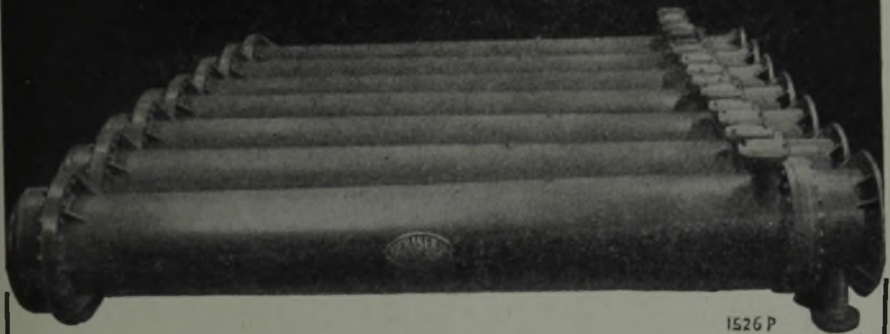
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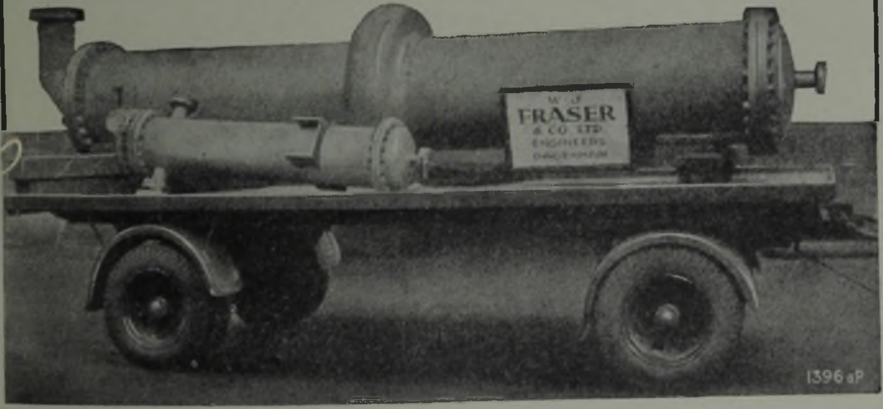
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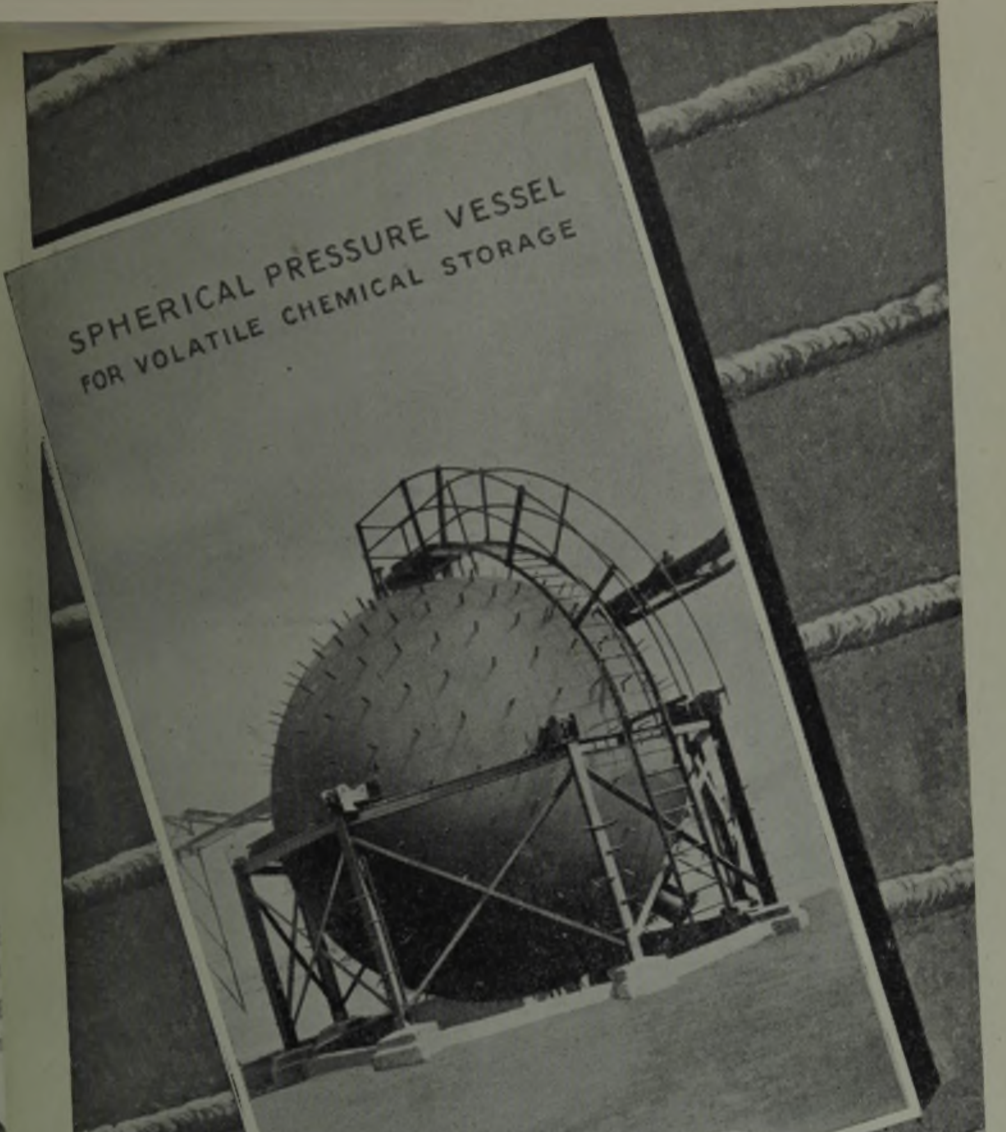

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