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OCTANE RATING RELATIONSHIPS OF ALIPHATIC, ALICYCLIC, MONONUCLEAR AROMATIC HYDROCARBONS, ALCOHOLS, ETHERS, AND KETONES.*

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THE modern internal-combustion engine owes the general smoothness of its performance to the quality of motor fuels used. There are many organic compounds which have boiling points within gasoline range which will run an automobile engine. The fuels operating to-day's engines are hydrocarbons derived from petroleum and natural gas. These gasolines have varying efficiencies that are expressed as octane ratings. The detonation properties of motor fuels are due to the type of organic molecules present, and their octane rating is a function of the structure and of the oxidation characteristics under high-temperature and pressure conditions. It should be pointed out that variation in engine conditions markedly alters the octane ratings of organic substances. Studies of the octane ratings, oxidation characteristics, and thermal stabilities of alkanes, alkenes, alkynes, cyclanes, cyclenes, mononuclear aromatics, alcohols, ethers, and ketones have been made in order to correlate the octane ratings of these compounds. Since modern synthetic processes have made individual hydrocarbons available in large volumes, their chemical structures have become increasingly important from a motor-fuel standpoint.

The relation of chemical structure to motor-fuel efficiency was first brought out in 1931, when Lovell, Campbell, and Boyd [1] published their work on the combustion properties of aliphatic hydrocarbons. These properties were reported as "aniline equivalents." In 1932 the octane-rating scale was officially established, following the work of Edgar [2] on synthesis of "*iso*-octane" and evaluation of mixtures of "*iso*-octane" in *n*-heptane.

The octane ratings of many pure hydrocarbons, alcohols, ethers, and ketones have been determined. The most extensive study so far attempted has been the work of the American Petroleum Institute, now starting the third year of its work in synthesis and determination of fuel qualities of pure hydrocarbons [3] boiling in the gasoline range. There are a number of pure hydrocarbons, alcohols, ethers, and ketones that have a higher antiknock value than *iso*-octane and could not be rated directly on the octane scale; hence they were extrapolated.

The research, motor, and four other proposed test methods for evaluating octane numbers of gasoline are shown in Table I.

Other factors, not mentioned in test-method specifications on which octane ratings are dependent, are valve and spark timing, manifold distri-

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TABLE I.

*Comparison of Operating Conditions for the Gasoline Knock Test Methods using the C.F.R. Engine as a Basis.**

All methods use 3¼-in. × 4½-in. variable compression cylinder, unless otherwise noted.

	Motor Method.	L-3 Method.	1939 Research Method.	Old Research Method.	C.F.R. Aviation Method (1940) (1-C).	Army Method (AN 9525) § (official for military service until Jan. 1941).
Speed.	Constant, 900 ± 9 r.p.m.	Constant, 900 ± 9 r.p.m.	Constant, 600 ± 6 r.p.m.	Constant, 600 ± 6 r.p.m.	Constant, 1200 ± 12 r.p.m.	Constant, 1200 ± 20 r.p.m.
Jacket temperature.	Constant, ± 1° F. Held between 209° and 215° F.	Constant, ± 1° F. Held between 209° and 215° F.	Constant, ± 1° F. Held between 209° and 215° F.	Constant, ± 1° F. Held between 209° and 215° F.	Constant at 374° ± 2° F. within ± 9° F.	Constant at 330° ± 2° F. within ± 5° F.
Spark advance.	Automatic, 26·0° at 5 : 1 compression ratio.	Automatic, 16° at 5 : 1 compression ratio.	Fixed, 13·0° for all compression ratios.	Automatic, 22·5° at 5 : 1 compression ratio.	Fixed, 35° for all compression ratios.	Fixed, 30° for all compression ratios.
Mixture temperature.	300° F. ± 2° F.	260° F. ± 2° F.	125° F. ± 2° F.†	Room temperature.†	Intake air 125° F. ± 5° F. Mixture temperature 220° F. ± 2° F.	Room temperature.†
Intake valve.	Shrouded.	Shrouded.	Shrouded.	Plain.	Plain.	Plain.
Fuel blends for checking engine.	49·1% C.P. benzene in A-6 equals 64·2% C-11 in A-6 (65 Oct. No.).	46·7% C.P. benzene in A-6 equals 63·5% C-11 in A-6 (65 Oct. (No.).	48·4% C.P. benzene in A-6 equals 72·5% C-11 in A-6 (70·0 Oct. No.).	65 Oct. No.	85% S-1 in M-2 vs. C.P. benzene to give same thermal plug reading.	88% *iso*-octane in *n*-heptane vs. C.P. benzene to give same thermal plug temperature.
Compression ratio for checking engine.‡	5·3 : 1.	5·5 : 1.	5·75 : 1.	5·3 : 1.	—	—
Instrumentation for determining knock.	Bouncing-pin and knockmeter.	Bouncing-pin and knockmeter.	Bouncing-pin and knockmeter.	Bouncing-pin and knockmeter.	Thermal plug.	Thermal plug.

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* J. S. Bogen, Universal Oil Products Company.

† This is the intake air temperature, not mixing temperature.

‡ This ratio must be corrected for barometer.

§ 2⅝-in. × 4½-in. variable compression cylinder.

bution, carburetion, air-fuel ratio, humidity, and engine conditions. Instantaneous pressures of 1200 psi or higher may occur under knocking conditions; temperatures in the cylinder may then range from 2200° to 2500° C. These conditions are highly significant when oxidation reactions are taking place. As a primary concept, octane ratings may be considered as the oxidation index of a given compound under the combustion conditions prevailing in an engine.

In considering the fundamental structural factors affecting the octane rating of organic compounds, there are a number of generalizations which may be extended to cover other compounds than hydrocarbons. A number of rules were proposed by Lovell, Campbell, and Boyd[4] in the study of hydrocarbons and their relation to anti-knock properties. For the pure hydrocarbons it was found necessary to modify somewhat their first and second generalizations, while consideration of data on the oxidized compounds showed that these rules were applicable to the oxidized class of motor fuels as well.

> *Rule* 1.—The longer the straight chain of carbon atoms contained in organic molecules, the lower the octane rating, with the exception of the alkenes, where ethene has a lower octane rating than the two following hydrocarbons.

The following examples in Tables II, III, and IV show the application of Rule 1 to the hydrocarbons of different series.

TABLE II.

Straight-chain Paraffins, Pure Compounds.

Compound.	Octane rating.	
	C.F.R. A.S.T.M.[3]	Research method.[5]
Methane	110	100
Ethane	104	100
Propane	100	100
Butane	92	95
Pentane	61	58
Hexane	25	34
Heptane	0	0
Octane	−17	—
Nonane	−45	—
Decane	—	−53

The octane ratings given by Smittenberg for the 2-alkenes do not follow the general smoothness of those reported by Lovell, Campbell, and Boyd in their work, nor do these values fall in line with Rule 1 as well as do the paraffins. Table III shows octane ratings for the pure olefins,[3] and Table IV shows octane ratings of the blends of pure olefins with a reference fuel. In general, it may be seen from the data in Table IV, the octane ratings of the blends follow the same trend as the pure compounds.

TABLE III.

Straight-chain Olefins, Pure Compounds.

Compound.	Octane rating,[3] C.F.R. A.S.T.M.
Ethene	81
Propene	85
Butene-2	83[6]
Pentene-2	80
Hexene-2	78
Octene-2	55

Calculated values of the octane ratings of olefins from aniline equivalents,[4] as well as the direct determination of octane ratings given by Smittenberg, Hoog, Moerbeek, and van der Zijden,[3] show the same trend in lowered rating with increase in chain length. The orientation of the double bond towards the centre of a molecule containing the same number of carbon atoms raises the octane rating.[4] Table IV shows the octane ratings determined on the pure compounds and on the blends of 1 gram mole of hydrocarbon per litre of 55 octane rating reference fuel.

TABLE IV.

Olefin Series,[10] Pure and Blended Compounds.

Compound.	Octane rating.			
	Pure compound.		Blended compound.	
	M.M.	R.M.	M.M.	R.M.
Ethene		100		85·5
Propene . . .		100		102·0
Butene-1 . . .	80			111·5
Butene-2 . . .	83			
Pentene-1 . . .		92		98·5
Pentene-2 . . .		98	107	125
Hexene-1 . . .		80		85
Hexene-2 . . .		89		100
Hexene-3 . . .		97		
Heptene-1 . . .		54		55
Heptene-2 . . .		70		
Heptene-3 . . .		84		95
Octene-1 . . .		39		25
Octene-2 . . .				55
Octene-3 . . .				73
Octene-4 . . .				91
Nonene-1 . . .				15

Data listed for the acetylene hydrocarbons are so scarce that no correlations can be made with the material; however, Table V shows the octane ratings determined for the straight-chain acetylenes, and Table VI shows a comparison of these acetylenes with straight chains to the olefins and paraffins of similar structure.

TABLE V.

Straight-chain Acetylenes, Pure and Blended Compounds.

Compound.	Octane rating, research method.	
	Pure compound.[7]	Blended compound.
Acetylene	80	
Pentyne-2		108[8]
Heptyne-1	84	76[9]
Heptyne-3	40	−30[7]
Octyne-2	66	62[9]

TABLE VI.

Pure and Blended Compounds.

Compound.	Octane rating, research method.	
	Pure compound.	Blended compound.
Ethane	>100[7]	
Ethene	>100[7]	85·5[9]
Ethyne	80[7]	
Pentane	58[11]	60[9]
Pentene-2	98[7]	125[9]
Pentyne-2		108[8]
Heptane	0[7]	0[9]
Heptene-1	54[7]	55[9]
Heptyne-1	84[7]	76[9]
Heptene-3	84[7]	95[9]
Heptyne-3	40[7]	−30[7]

While the data presented here are not too conclusive, it seems that the octane-rating effect of the acetylene bonding is intermediate between that of the paraffin bond and the olefin bond.

The pure compounds of the *cyclo*paraffin and aromatic series given in Table VII also follow Rule 1 insofar as the data are given; that is, the length of the substituting straight chain lowers the octane rating.

TABLE VII.

Compound.	Octane rating, C.F.R. A.S.T.M.
*cyclo*Pentane	83[3]
Methyl*cyclo*pentane	82[3]
*cyclo*Hexane	77[3]
Methyl*cyclo*hexane	71[3]
Benzene	108[3]
Methylbenzene (Toluene)	104[3]
Ethylbenzene	96[12]

The values derived from calculating aniline equivalents in blends for the alicyclic group show the trend even better than those determined for the pure compound. Table VIII shows the octane ratings for the *cyclo*-paraffin series.

TABLE VIII.

cyclo*Paraffin Series,*[10] *Pure and Blended Compounds.*

Compound.	Octane rating, research method.	
	Pure compound.	Blended compound.
*cyclo*Pentane	100	125
Methyl*cyclo*pentane	81·5	71
Ethyl*cyclo*pentane	62	59
Propyl*cyclo*pentane		16
Butyl*cyclo*pentane		−11
Pentyl*cyclo*pentane		−19
*cyclo*Hexane		86
Methyl*cyclo*hexane		74
Ethyl*cyclo*hexane		44
Propyl*cyclo*hexane		20
Butyl*cyclo*hexane		3
Pentyl*cyclo*hexane		−8

Table IX shows *cyclo*-olefines, and here also the effect of chain lengthening is evident.

TABLE IX.

cyclo*Olefin Series,*[10] *Blended Compounds.*

Compound.	Octane rating, research method, blended compound.
*cyclo*Pentene	140
Methyl*cyclo*pentene	143
Ethyl*cyclo*pentene	102
Propyl*cyclo*pentene	96
Butyl*cyclo*pentene	82
Pentyl*cyclo*pentene	63
*cyclo*Hexene	102
Methyl*cyclo*hexene	133
Ethyl*cyclo*hexene	100
Butyl*cyclo*hexene	63
Pentyl*cyclo*hexene	58

The monoalkyl-substituted series of aromatic hydrocarbon blends shows a deviation from Rule 1 on the longer straight-chain lowering of octane ratings. Table X shows that up to propylbenzene the octane rating rises with increasing chain length; beyond the propyl group, however, the normal lowering with progressive chain lengthening[14] is exhibited. This seems to be true only for the blends, since Table VII, on pure compounds, shows the lowering of octane rating with each successive methyl addition to the alkyl substitution group.

TABLE X.

Blended Compounds.[13]

Compound.	Octane rating, research method, blended compound.
Benzene	108
Methylbenzene	120
Ethylbenzene	128
Propylbenzene	137
Butylbenzene	115
Pentylbenzene	101
Heptylbenzene	46

Rule 2.—Branched chain aliphatic compounds have higher octane ratings than the normal compounds.

(*a*) Monomethyl isomers have higher octane rating than the normal compound, and the dimethyl isomers are higher than either the normal or monomethyl isomers, as shown in Table XI.

TABLE XI.

Compound.	Octane rating,[3] C.F.R. A.S.T.M.
Hexane	25
2-Methylpentane	73
3-Methylpentane	75
2 : 2-Dimethylbutane	96
2 : 3-Dimethylbutane	95

(*b*) As the monomethyl substitution approaches the centre of the molecule, the octane rating is increased over that of the other monomethyl substitutions located nearer the end of the chain; for example, 2-methylpentane has an octane rating of 73 and 3-methylpentane a rating of 75 in the group of hydrocarbons shown in Table XII. This is further substantiated in blending values given for 2-methylpentane, 69; and 3-methylpentane, 84.[14] Lovell and Campbell state that centralization of the molecule is the factor increasing the octane rating; however, this is not true in the case of the dimethyl compounds, where one carbon atom contains both methyl substituents.

TABLE XII.

Compound.	Octane rating,[3] C.F.R. A.S.T.M.
2-Methylpentane	73
3-Methylpentane	75

Branching of the side-chains in the olefinic series shows the same effect as the paraffin branching. The presence of the double bond in its various positions is also seen to influence the octane rating of the olefins.

Tables XIII and XIV show the same effects in the olefin series as were discussed in the paraffin group, with some exceptions showing, due possibly to the type of linkages, and not the structure. Table XIII shows a higher octane rating for peripheral methyl substitutions where the double bonds lie near the centre, in this instance in the 2-position, while for paraffin hydrocarbons the substitution of methyl radical near the centre of the molecule raises the octane rating.

TABLE XIII.

Pure and Blended Compounds.

Compound.	Octane rating.		
	Pure compound, motor method.	Blended compound.	
		Motor method.	Research method.
3-Methylpentene-2			109 [9]
4-Methylpentene-2			115 [7]
2 : 4 : 4-Trimethylpentene-2	89 [7]	133 [9]	
3 : 4 : 4-Trimethylpentene-2	85·6 [15]	72·5 [15]	

The olefin compounds having double bonds in the one position give octane relations more nearly like the paraffins in this instance, since the methyl substitutions near the centre of the molecules give higher ratings as in the paraffin series. Table XIV shows the 1-alkenes in this relation.

TABLE XIV.

Pure and Blended Compounds.

Compound.	Octane rating.			
	Pure compound.		Blended compound.	
	M.M.	R.M.	M.M.	R.M.
4-Methylhexene-1		85 [7]		86 [9]
5-Methylhexane-1		82 [7]		83 [9]
2-Methyloctene-1	74·8 [15]		69·8 [15]	
3-Methyloctene-1	83·5 [15]		72·2 [15]	

Table XV, on the acetylenes, shows a lowering of the octane rating with the orientation of the triple bond towards the centre of the molecule which is directly opposite the effect noted in the case of the olefines.

TABLE XV.

Pure and Blended Compounds.

Compound.	Octane rating, research method.	
	Pure compound.	Blended compound.
Heptyne-1	84 [7]	76 [9]
Heptyne-3	40 [7]	−30 [7]
5-Methylhexyne-1		89 [9]
5-Methylhexyne-2		88 [8]

(*c*) Dimethyl substitutions exhibit the same tendencies as the monomethyl substitutions, as long as the two methyls are on adjacent carbon atoms in the molecule. 2 : 3-Dimethylhexane has an octane rating of 76 and 3 : 4-dimethylhexane has a value of 85. Table XVI shows the ratings in tabular form.

TABLE XVI.

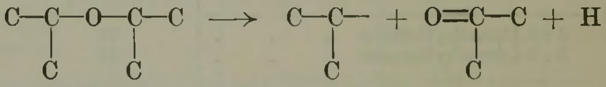
Compound.	Octane rating,[3] C.F.R. A.S.T.M.
2 : 3-Dimethylhexane	76
3 : 4-Dimethylhexane	85

These types of methyl branching introduce tertiary carbon atoms into the molecule, and the effect is one of diminishing the ease of oxidation.[16]

In explaining the higher octane ratings of monomethyl isomers and the rise in rating accompanying the movement of methyl groups towards the centre of the molecule, the thermal behaviour of normal and *iso*butane and of normal and *iso*pentane is relevant.

Under comparable conditions (600–700° C.) *iso*butane dehydrogenates more readily to *iso*butene than *n*-butane to butenes.[17] In the case of normal and *iso*pentane, the *iso*-compound was shown to yield alkenes with the double bond in the inner rather than the terminal position found in the thermal decomposition products of the normal compound.[18] Since the final products of a purely thermal reaction are shown to be olefins, the intermediate products formed at high temperatures and pressures could readily be the free radicals derived from the parent compound. Experimental evidence has shown that the energy required to dissociate the C–C bond is about 21,000 cal. less than that required for the C–H bond break. Dissociation energies for C–C and C–H bonds are 71,000 and 92,000 cal., respectively. In the case of oxidation reactions at explosion temperatures, Sagulin [19] found the heat of activation of the C–H bond to be about 64,000 cal., which accounts not only for the ease of dehydrogenation, but would, in part, explain the much higher octane ratings of the isomeric compounds in relation to the straight chain. Even at explosion temperatures it may be postulated that the momentary formation of the free radicals, *iso*propyl and *iso*butyl, reduces the volume of gases simultaneously released in the engine cylinder. In contrast, there are many more radicals, and hence greater volumes, in the case of the straight-chain compounds.

A plausible explanation for the higher anti-knock rating of the hydrocarbons with the centred methyl would be a split of the hydrocarbon molecule at the tertiary carbon atom, producing an anti-knock effect which would give two, or possibly three, parts of the molecule instituting chain reactions at the same time in contrast to the number of radicals released by the normal compound. The pressure increase set up by the splitting of the molecule gives the knock effect in accordance with the number and kind of hydrocarbon radicals set free. According to Rice's explanation, the pressure existing in the automotive cylinder would be conducive to the formation of free *iso*propyl and *tert.*-butyl radicals.[20] As a further observation it may also be stated that ketones[21] might be reasonably expected under those pressure and temperature conditions existing in the automotive cylinder. Both the oxygen and the hydrocarbon are in an activated state, and in the case of the isomeric hydrocarbons the ketone would also have a higher initial combustion temperature, and therefore greater stability, than the peroxides which are postulated by Lewis and von Elbe.[22] A further explanation might be given in the justification of the high anti-knock rating for *iso*propyl ether, which is 99. In this instance, with one part of the molecule having an oxygen attached, the reaction might be shown to proceed as follows :



$$\mathrm{C{-}\underset{\substack{|\\ C}}{C}{-}O{-}\underset{\substack{|\\ C}}{C}{-}C \longrightarrow C{-}\underset{\substack{|\\ C}}{C}{-} + O{=}\underset{\substack{|\\ C}}{C}{-}C + H}$$

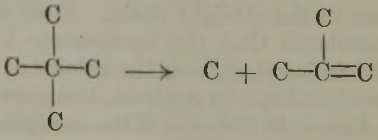
Such a compound would oxidize at the tertiary carbon in one part of the ether, whilst the other part of the ether would have formed a ketone.

Rule 3.—A quaternary carbon atom when oriented towards one end of a hydrocarbon chain increases the octane rating. Table XVII shows the effect of orientation of the quaternary carbon.

TABLE XVII.

Compound.	Octane rating, C.F.R. A.S.T.M.
2 : 2-Dimethylpentane . . .	93[3]
3 : 3-Dimethylpentane . . .	84[3]
2 : 2 : 3 : 3-Tetramethylhexane .	97[23]
3 : 3 : 4 : 4-Tetramethylhexane .	65[24]

The effect of the quaternary carbon under purely thermal conditions has not been sufficiently studied to give basis to any such hypotheses as were given for the effect of the tertiary carbon. Frey and Hepp[18] found that neopentane decomposed almost quantitatively at 575° C., according to the following reaction :



$$\mathrm{C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}C \longrightarrow C + C{-}\overset{\substack{C\\ |}}{C}{=}C}$$

If this reaction may be applied as affecting other compounds of this type, the initial reaction may be shown as a splitting of the molecule at the quaternary carbon. 2 : 2-Dimethylpentane will possibly react to give either the olefin, or more probably to give the free radicals, thus releasing only two gases in the engine cylinder. The pressure increase set up by such a yield of products of decomposition would be much less than that released by the isomeric 3 : 3-dimethylpentane, and this would explain, in part, the reduced octane rating for the 3 : 3-dimethyl compound. This assumption is based on Rice's [20] statement that under heat and pressure conditions heavier radicals such as *tert.*-butyl and *iso*propyl may momentarily exist. In 3 : 3-dimethylpentane, with the quaternary carbon centred in the molecule, the octane rating is 84, in comparison with 93 for the 2 : 2-dimethyl compound. In view of Rice's explanation of the more radicals set free the higher the initial pressure, it may be shown that three gaseous products would be formed in the case of the 3 : 3-dimethyl compound rather than two as was shown for the 2 : 2-dimethyl compound. The pressure increase thus set up would probably institute the knocking more readily than in the other compound.

Orientation of compacted dimethyl and trimethyl substitutions towards one end of the molecule raises the octane rating as shown in Table XVIII.

TABLE XVIII.

Compound.	Octane rating,[3] C.F.R. A.S.T.M.
2 : 2-Dimethylbutane . . .	96
2 : 3-Dimethylbutane . . .	95
2 : 2-Dimethylpentane . . .	93
2 : 3-Dimethylpentane . . .	89
2 : 4-Dimethylpentane . . .	82
3 : 3-Dimethylpentane . . .	84
2 : 3-Dimethylhexane . . .	76
2 : 5-Dimethylhexane . . .	52
3 : 4-Dimethylhexane . . .	85
2 : 2 : 3-Trimethylpentane . .	102
2 : 2 : 4-Trimethylpentane . .	100
2 : 3 : 4-Trimethylpentane . .	97

Rule 4.—Methyl additions on cyclic structures of a given number of carbon atoms lower the octane rating, whilst methyl additions on a chain of a given number of carbon atoms raise the octane rating, except in the case of *n*-butane to 2-methylbutane, where the octane rating is lowered by adding the methyl substituent. Table XIX shows the relationship.

Rule 5.—In hydrocarbons of the *cyclo*hexyl group the effect of the *ortho*, *meta*, and *para* positions is one of lowering the octane rating as the substituents are more widely separated. The *ortho* position gives the highest octane rating, and the *para* position gives the lowest. In the benzene series the opposite effect is noted for the *ortho*, *meta*, and *para* positions. Tables XX and XXI show the effect of position for *cyclo*hexane and benzene hydrocarbons.

TABLE XIX.

Compound.	Octane rating,[3] C.F.R. A.S.T.M.
n-Butane	92
2-Methylbutane	89
n-Pentane	61
2-Methylpentane	73
3-Methylpentane	75
n-Hexane	25
2-Methylhexane	45
n-Heptane	0
3-Methylheptane	35
*cyclo*Pentane	83
Methyl*cyclo*pentane	82
*cyclo*Hexane	77
Methyl*cyclo*hexane	71
Benzene	108
Methylbenzene (Toluene)	104

TABLE XX.

Pure and Blended Compounds.[10]

Compound.	Octane rating, research method.	
	Pure compound.	Blended compound.
ortho-1 : 2-Dimethyl*cyclo*hexane	86	75
meta-1 : 3-Dimethyl*cyclo*hexane	77	68
para-1 : 4-Dimethyl*cyclo*hexane	74	75
1-Methyl-2-ethyl*cyclo*hexane	74	55
1-Methyl-3-ethyl*cyclo*hexane	58	34
1-Methyl-4-ethyl*cyclo*hexane	54	27
1-Methyl-2-propyl*cyclo*hexane	49	37
1-Methyl-3-propyl*cyclo*hexane	39	22
1-Methyl-4-propyl*cyclo*hexane	34	20
1-Methyl-2-butyl*cyclo*hexane	39	6
1-Methyl-3-butyl*cyclo*hexane	34	−5
1-Methyl-4-butyl*cyclo*hexane	28	−5

TABLE XXI.

Blended Compounds.[10]

Compound.	Octane rating, research method, blended compound.
ortho-1 : 2-Dimethylbenzene	121
meta-1 : 3-Dimethylbenzene	144
para-1 : 4-Dimethylbenzene	154
1-Methyl-2-ethylbenzene	107
1-Methyl-3-ethylbenzene	130
1-Methyl-4-ethylbenzene	147
1-Methyl-2-propylbenzene	114
1-Methyl-3-propylbenzene	130
1-Methyl-4-propylbenzene	130
1-Methyl-2-butylbenzene	102
1-Methyl-3-butylbenzene	113
1-Methyl-4-butylbenzene	123
1-Methyl-2-amylbenzene	90
1-Methyl-3-amylbenzene	90
1-Methyl-4-amylbenzene	100
1 : 3-Diethylbenzene	145
1 : 4-Diethylbenzene	158

ALCOHOLS, ETHERS, AND KETONES.

Oxidation compounds derivable from the hydrocarbons have been considered for some time as products suitable for motor fuels, and in some instances have been widely adopted, although these compounds have not proved entirely satisfactory. Ketones and ethers have been given some attention, but they have not had as wide application as the alcohols.

The following tables and generalizations show the relative octane rating efficiencies of these compounds.

> *Rule* 6.—With the exception of methyl alcohol, the lengthening of the straight chain of carbon atoms in the alcohol molecule lowers the octane rating.

Table XXII shows the octane ratings of the normal alcohols up to pentyl alcohols.

TABLE XXII.

Alcohols.[25]

Compound.	Octane rating, C.F.R. motor method, pure compounds.
Methyl	98
Ethyl	99
n-Propyl	90
n-Butyl	87
n-Pentyl	78

Up to and inclusive of *n*-butyl alcohol, the effect of the OH radical seems to be one of lowering the octane rating in comparison with the normal hydrocarbons. Pentyl alcohol shows a higher octane rating than *n*-pentane; however, at present there are no data to show whether or not this reversal holds for the remainder of the normal alcohols boiling within the gasoline range.

Isomeric alcohols show that chain branching raises the octane rating, which is in direct agreement with Rule 2 shown previously for the hydrocarbons. Table XXIII shows the *n*-alcohols and their isomers and the effect of chain branching on octane number.

TABLE XXIII.

Alcohols.

Compound.	Octane rating, C.F.R. motor method.[25]
n-Propyl	90
*iso*Propyl	104
n-Butyl	87
*iso*Butyl	88
sec.-Butyl	92
tert.-Butyl	100+
n-Amyl (pentyl)	78
tert.-Amyl (pentyl)	100+

The octane ratings of a number of pure ketones have been determined, and, insofar as the data show, the same rules hold for the ketones as for the alcohols. Table XXIV shows the octane ratings of the ketones.

TABLE XXIV.

Ketones.

Compound.	Octane rating, C.F.R. motor method.
Methyl (acetone)	100
Methylethyl	99
Methylpentyl	80
4-Methyl-3-penten-2-one	91
2 : 6-Dimethyl-2 : 5-heptadien-4-one	78

The two latter compounds in Table XXIV are not strictly comparable to the preceding ones in the table, but they serve to show somewhat the effect of branching and the effect of the double bond; however, there is no method in this instance of determining the separate effect of either type of structure.

The material presented for the ethers is not on the pure compounds, but was taken from 25 per cent. blends of the pure ethers in aviation gasoline of 74 octane number.[26] The figures of over 100 octane number are extrapolated values.

Tables XXV and XXVI show the effect of chain lengthening and chain branching in ethers which is analogous to that of the preceding compounds, with the exception of the ethyl-substituted compound; in each case the octane rating is higher than the methyl compound preceding. There was a slight indication of this phenomenon in the alcohols, but it was not nearly so marked as in the case of the ethers.

TABLE XXV.

Ethers.[26]

Compound.	Octane rating, C.F.R. motor method, blended compound.
Methyl*iso*propyl	73
Ethyl*iso*propyl	75
Methyl-*tert.*-butyl	111
Ethyl-*tert.*-butyl	115
n-Propyl-*tert.*-butyl	103
n-Butyl-*tert.*-butyl	81
n-Amyl-*tert.*-butyl	63
Methyl-*tert.*-amyl	108
Ethyl-*tert.*-amyl	112

TABLE XXVI.

Effect of Branched Chain in Ethers.

Compound.	Octane rating, C.F.R. motor method, blended compound.
Ethyl-*sec.*-butyl	63
Ethyl-*tert.*-butyl	115
n-Butyl-*tert.*-butyl	81
sec.-Butyl-*tert.*-butyl	106

From the foregoing tables on the octane rating of alcohols, ketones, and ethers, it is readily seen that these oxygenated compounds follow approximately the same rules on octane rating relationships as the paraffin hydrocarbons.

THERMAL RELATIONSHIPS AND OCTANE RATINGS.

The octane ratings and the relationships due to structure presented for the hydrocarbons are not unique, since other types of constants have shown that thermal stabilities, initial combustion temperature, and critical compression ratios are also characteristic functions of the structure involved, and are lowered with the increased chain lengths.

Rule 7.—The thermal stability of the pure normal paraffins is inversely proportional to the length of the carbon chain.[27]

The following rules are more or less dependent on Rule 6, yet their applicability in engine performance is more readily seen.

Rule 8.—The initial combustion temperature is lowered as the carbon content of the normal paraffin increases.

Table XXVII shows the lowered initial combustion temperatures with increased carbon chain length.

TABLE XXVII.

Lowest Temperatures of Initial Combustion in Air of Normal Paraffin Hydrocarbons Compared to their Octane Ratings.[28]

Compound.	Initial combustion temperature, ° C.	Octane rating.	
		Motor method.	Research method.
Methane . . .	615	125	100
Ethane . . .	542	125	100
Propane . . .	420 *	125	100
Butane . . .	350 *	91	95
Pentane . . .	295	64	58
Hexane . . .	265	59	34
Heptane . . .	230 *	0	0
Octane . . .	215	−28	
Nonane . . .	210	−28	
Decane . . .	210		−53

* These values were interpolated from a curve which was plotted from the other values shown giving temperatures of initial combustion against the number of carbon atoms in the normal paraffin chains.

Rule 9.—The critical compression ratio of the pure normal alkanes is in inverse order to the carbon chain length, *i.e.*, the highest critical compression ratios are for the lower members of the series.

Tables XXVIII and XXIX show the critical compression ratios for the various hydrocarbons as well as the actual operating compression pressures for the test engine and for the automobile engines under approximate test-engine conditions.

TABLE XXVIII.

Paraffins.	Critical compression ratio.	Compression pressure, P.S.I.	
		Actual values C.F.R. engine.	Auto engine under approximate C.F.R. conditions.
Methane . .	15 : 1	349	419
Ethane . . .	14 : 1	323	388
Propane . .	12 : 1	273	327
Butane . . .	6·4 : 1	130	156
Pentane . .	3·8 : 1	67	78
Hexane . .	3·3 : 1	55	66
Heptane . .	2·8 : 1	42	50

TABLE XXIX.

Olefins.	Critical compression ratio.	Compression pressure, P.S.I.	
		Actual values C.F.R. engine.	Auto engine under approximate C.F.R. conditions.
Ethene	8·5 : 1	188	226
Propene	8·4 : 1	185	222
Pentene-1	5·8 : 1	115	138
Hexene-1	4·6 : 1	82	98
Heptene-1	2·8 : 1	42	50

SUMMARY.

In summarizing the effect of chemical structures on octane ratings, the combustion conditions under which the octane ratings have been made are the most vital factor in any octane rating given for a chemical compound. The octane ratings given for the various compounds and the generalizations made from them are specific for the test method indicated, and any change in the test method markedly alters the octane rating of the compound.

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THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute was held at the Royal Society of Arts, London, W.C. 2, at 5 p.m., on Tuesday, March 11th, 1941. The Chair was occupied by Dr. F. H. GARNER.

The following paper was introduced by Dr. A. E. DUNSTAN, and on his proposition it was agreed that a cable should be sent to Dr. Egloff, saying that his paper had been presented that evening and tendering him the thanks of the Institute for it.

"Octane Rating Relationships of Aliphatic, Alicyclic, Mononuclear Aromatic Hydrocarbons, Alcohols, Ethers, and Ketones." By Gustav Egloff and P. M. Van Arsdell. (See page 121.)

DISCUSSION.

THE CHAIRMAN said he was sure all the members present would agree that the authors were to be congratulated on having Dr. Dunstan to present their paper for them, and he wished to propose a vote of thanks to Dr. Dunstan for presenting the paper in his own inimitable manner.

The paper was largely a compilation of the octane ratings scattered throughout the literature of hydrocarbons, alcohols, ethers, and ketones—in fact, practically all the compounds that were likely to be met in motor fuel. The ratings were mainly by the motor method, and, to use Dr. Dunstan's words in introducing the paper, the really important question was what the engine thought of the fuel. To answer that question fully one had to know, of course, not only the rating by the motor method, but also the rating under other engine conditions if satisfactory correlation was to be obtained with actual performance in the motor-car or in the aero engine. For that reason, the American Petroleum Institute had recently sponsored a programme of research on hydrocarbons, and had just published a report of twenty-three pure hydrocarbons, and had employed two different speeds, two different jacket temperatures, two different air temperatures, and different concentrations of lead tetraethyl.

He did not think the authors' statement: "The relation of chemical structure to motor-fuel efficiency was first brought out in 1931, when Lovell, Campbell and Boyd published their work on the combustion properties of aliphatic hydrocarbons," was quite correct, because the work of Ricardo and others preceded that work by a number of years. Actually the work of Ricardo and the work of Boyd and his co-workers in the States were practically contemporary, but it was Ricardo who first investigated the individual hydrocarbons present in motor fuels, particularly benzene, toluene, and xylene, which was included in the Empire Motor Fuels Committee Report published in 1924. This was supplemented later by an investigation made into cracked fuels under the auspices of the Institution of Automobile Engineers.

THE CHAIRMAN then read the following comments by the President, Professor Nash:—

"The paper by Messrs. Egloff and Van Arsdell is a very interesting one indeed, and I do not envy Dr. Dunstan the task of having to present it to the members of the Institute.

There are a few point I should like to raise, and the first one is in connection with Table III, where it will be noticed there is a diminution from hexene-2 octane rating 78 to octene-2 octane rating 55, that is, a difference of 23 octane numbers, which does not fall into line with the diminution of octane rating from propene upwards. It causes one to doubt the purity of the octene-2 and to suggest that the double bond is probably nearer to the centre of the molecule.

With regard to Table VI, the first heptyne-1 should undoubtedly read heptene-1. With the C_5 hydrocarbons it will be noticed that there is a decrease of the octane rating in the blended compound, whereas with the C_7 hydrocarbons there is an increase. It is very difficult to prove the position of the triple and double bonds, and causes one to query again the purity of the substances tested.

In the paragraph preceding Table VIII reference is made to aniline equivalents in blends, and I should like to ask whether this method has been proved to be an accurate one. It would also be interesting to know in the *cyclo*-olefine series in Table IX where the position of the double bond is. A comparison is also made between Table X and Table VII, the former being for blended compounds and the latter for pure compounds. As there would be a difference here in the primary products of combustion, could one expect these two tables to be exactly comparable ?

In the case of Table XIII centralization of the methyl radical appears to decrease the octane rating, whereas when it is in the peripheral position the octane rating increases. The reverse, however, is the case with the compounds in Table XIV. Can we make a generalization out of the data available, which rather suggests in regard to Table XIV that the compounds are acting oppositely ? In regard to Table XVIII can one differentiate between an octane rating of 96 and 95 ? In Rule 5 hydrocarbons of the *cyclo*-hexyl (*sic*) group are compared with the benzene series. This rule is not so remarkable when one bears in mind that the two cyclic groups are entirely different. Again, one would ask whether, as in Table XXIII, one can differentiate the behaviour of the *n*-butyl and *iso*-butyl alcohols when the octane ratings are 87 and 88 respectively."

Dr. A. E. Dunstan said that it had struck him that some of the figures might be open to some misapprehension, because before the combustion process, as the authors pointed out, the hydrocarbon or alcohol or ketone might be subjected to very high temperatures ; the authors mentioned 2200° C. He did not know whether that was a justifiable temperature, in the sense that it was uniform throughout the mixture.

The Chairman said it was quite feasible.

Dr. Dunstan suggested that there was therefore a very great possibility of isomerization taking place ; at any rate, he thought that was a point which should be borne in mind. Did the authentic chemical entity exist under such conditions or was it changed ?

Dr. E. B. Evans regretted that he had not yet had the opportunity to study Dr. Egloff and Mr. van Arsdell's interesting paper in detail. There were no points which he himself wished to raise at the moment, but he noticed that Professor Nash had raised a question as to the accuracy of the method of calculating blending octane numbers from aniline equivalents.

This calculation, which enabled Campbell, Lovell, and Boyd's results to be expressed in terms of octane numbers, was made about 1932, and published in a paper by Dr. Garner and others (Garner, Evans, Sprake, and Broom, *Proceedings of World Petroleum Congress*, 1933, p. 170). The aniline equivalents were determined by an engine and method approximating to the old C.F.R. Research Method, using for the blends a base fuel of octane number 55. Knowing the blending octane numbers and aniline equivalents of *n*-heptane and *iso*-octane, two straight lines were drawn giving the relation between the blending octane numbers and aniline equivalents of 20 per cent. volume solutions of these hydrocarbons. A number of the hydrocarbons for which aniline equivalents had been recorded by Campbell, Lovell, and Boyd had also been examined for blending octane number on the S. 30 engine at 212° F. jacket temperature, by ourselves. The S. 30 procedure is very similar to the old C.F.R. Research

Method, and plotting the data from the two sources showed that most of the points fell very near to the two straight lines obtained from heptane, *iso*-octane, and the reference fuel. Full details of the method of conversion are given in the paper referred to, and the indications are that there is considerable justification for the converted values.

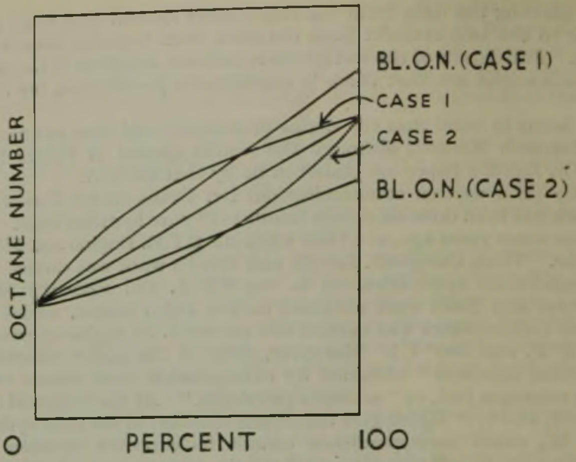
It must be borne in mind that the engine procedures used were not exactly those of the C.F.R. Research Method, although the results quoted in Tables IV, VII, IX, etc., etc., of Dr. Egloff's paper are stated to be by that method.

Subsequently (in a written communication) Dr. Evans stated that a considerable amount of work has been done on octane numbers of pure hydrocarbons. Most of this was carried out some years ago, at a time when the C.F.R. Engine and Motor Methods were not in use. Thus, Campbell, Lovell, and Boyd's work was carried out using an engine and conditions approximating to the C.F.R. Old Research Method. The results of Howes and Nash were obtained on the Delco engine, whilst the work of Garner and his collaborators was carried out on the S. 30 engine at two jacket temperatures (212° F. and 300° F.). Moreover, most of the earlier results were either " blending octane numbers " obtained by extrapolation from blends of the hydrocarbon with a reference fuel, or " aniline equivalents." As the results of Smittenberg, Hoog, Moerbeck, and v. d. Zijden give the octane numbers of the pure hydrocarbons by the C.F.R.M.M., exact correspondence cannot be expected between the various figures quoted by Dr. Egloff and Mr. van Arsdell. This is particularly so in the cases of aromatic and unsaturated hydrocarbons, where the curves of octane number against percentage hydrocarbon in the reference fuel are far from linear. Table XX for naphthene hydrocarbons also illustrates the differences that may be obtained. As in general the concentration of individual hydrocarbons does not exceed a small percentage, except where aromatic or *iso*-paraffin hydrocarbons are used as blending agents, the " blending octane number " is of more practical significance than the rating of the pure hydrocarbon, when considering the usual type of fuel, whilst the values for certain pure hydrocarbons assume importance in connection with aviation fuels of high octane number. Having regard to the different techniques of determination and methods of expression of results employed, it is gratifying to find that the general rules relating knock-value and structure hold as widely as they do.

Dr. A. J. V. Underwood agreed that the authors and Dr. Dunstan had rightly stressed the dependence of the octane number on the conditions of test. This was clearly shown by a comparison of Tables VII and X. In Table VII the figures for benzene, methylbenzene, and ethylbenzene were given as 108, 104, and 96, respectively. In Table X, using a different method of rating and giving blending values, the corresponding figures were 108, 120, and 128. Thus the value for benzene remained unchanged at 108 in the two different tests, whilst the *value* for ethylbenzene rose from 96 to 128. To express it quantitatively very roughly, ethylbenzene was some 20 per cent. better than benzene, according to Table X, whilst according to Table VII it was 10 per cent. worse than benzene. Again, in Table XIII the figures for 2 : 4 : 4-trimethylpentene-2 and for 3 : 4 : 4-trimethylpentene-2 were given as 89 and 85·6 respectively for the pure compound, using the motor method, whilst for the blended compound, using the same method, the corresponding figures were 133 and 72·5. There might be another factor apart from the different test conditions—namely, even though they were presumably using the same method. He thought the decimals might well be omitted in quoting these octane ratings, as they suggested a degree of accuracy which was not justified.

Mr. J. S. Jackson commented on the fact that octane numbers such as 74·8, 69·8, 72·2 appeared in the paper. Such published figures tended to give a rather false impression of the accuracy attainable with the C.F.R. engine, and he felt that these figures should have been rounded off and reported as 75, 70, and 72, respectively. He also pressed for the general acceptance of one method of test for the determination of octane numbers.

The Chairman thought the explanation of the point raised by Dr. Underwood was to be found partly in the shape of the octane number curves of blends of hydrocarbons.



Blending curves may be (1) above, or (2) below a straight line joining the octane number of the two hydrocarbons or (3) a straight line joining the two octane numbers. With hydrocarbons of type 1 the blending octane number is higher than that of the straight hydrocarbon, with type 2 lower, and with type 3 the same. This subject was fully discussed in a paper before the World Petroleum Congress in 1933. (The Blending Octane Numbers of Pure Hydrocarbons and their Dependence upon Concentrations: by Garner, Evans, Sprake, and Broom.)

The Chairman said that any written contributions to the discussion which were sent in to the Institute would be forwarded to Dr. Egloff, who would reply to them as well as to the remarks which had been made that evening.

The vote of thanks to Dr. Dunstan was carried unanimously, and the meeting then terminated.

STUDIES ON THE SEPARATION OF PARAFFIN WAXES.

PART IV.—THE SWEATING OF WAX-OIL MIXTURES.*

By M. F. Sawyer, Ph.D., A.M.Inst.Pet., T. G. Hunter, D.Sc., F.Inst.Pet., and A. W. Nash, M.Sc., F.Inst.Pet.

It has been indicated previously [3] that an investigation of the factors affecting the efficiency of the sweating process in which the same oil and wax stock, and also the same sweater, are used throughout, resolves itself into a consideration of the effects of the following variables :—

(1) The amount of oil in the oil–wax mixture,
(2) The rate of sweating,
(3) The rate and extent of the cooling of the oil–wax mixture before commencing to sweat, and
(4) The viscosity of the oil.

No account of experiments on the sweating of synthetic oil–wax mixtures has so far appeared in the technical literature. An objection to the use of such mixtures is that they are not obtained directly from the crude in the relative amounts in which they are blended. The composition of the stock is, however, immaterial, as it is possible that such a stock could be obtained from a crude. Moreover, there are certain definite advantages attending the use of synthetic mixtures.

Complications due to the variations in composition of the waxes and oils present in the mixture, such as might be encountered when using distillates of different boiling ranges, are eliminated. There is also no longer the necessity for the determination of the oil content of the stock—a matter of some difficulty. In the present instance the possible yields of the various melting-point waxes that may be obtained from the wax stock are already known from the previous fractional melting experiments. Finally blends of any desired oil content may be prepared very easily.

Oil Stock.

The stock of dewaxed oil, which was, of course, essential for this series of experiments, was prepared in the following manner. Dewaxed Second Cooled Blue Oil from the Llandarcy Refinery of the Anglo-Iranian Oil Co. was used as the starting material for the preparation. This oil had been removed from the wax distillate cut by filter pressing at a temperature of 13° F. during the normal refinery processing of the distillate, and was further dewaxed in the laboratory with ethylene dichloride at −30° C., using a leaf-filter type dewaxing apparatus.

The oil-solvent mixture containing one volume of oil to two volumes of

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* Paper received 23rd January, 1941.

solvent was cooled to −30° C., and then filtered from the wax deposited at this temperature. The solvent was removed from the oil by distillation under reduced pressure with a continuous stream of nitrogen passing through the liquid. The wax-free oil had the following properties :—

Specific gravity at 60° F.	0·8960
Refractive index at 60° F.	1·4867
Cloud point	Below −5° C.
Viscosity :—	
Redwood I at 100° F.	64·1 secs.
Redwood I at 140° F.	46·7 secs.

WAX STOCK.

The wax stock was that of melting point 122·1° F. used in the experiments on fractional melting described in previous publications.[2,3]

EFFECT OF OIL CONTENT.

In order to investigate the effect of oil content on the sweating operation, six synthetic wax–oil mixtures containing respectively 2, 5, 10, 20, 30, and 40 per cent. by weight of oil were prepared.

The desired amounts of wax and oil were weighed into a beaker. The mixture was then liquefied, thoroughly stirred, and the sample prepared in the sweater as previously described.[3] A sweating rate of 5 per cent. per hour was employed. This rate, besides being likely to lead to satisfactory results, was also quite convenient, as it enabled a sweating run to be completed in two days. The temperature of the sample in the sweater was gradually increased from room temperature, the time elapsing before the collection of the first drops of liquid phase being dependent on the amount of oil in the sample. This is illustrated in Table I.

TABLE I.

Oil content of sample, %.	First drops of liquid phase after.	Temperature of mass, ° F.
2	210 mins.	101
5	180 ,,	81
30	30 ,,	69
40	10 ,,	65

From the stage at which the first drops of liquid appeared, the heating was adjusted so that sweating proceeded at the desired rate. For the wax–oil mixtures of higher oil content only slight heating was required to maintain the rate during the collection of the first 10 per cent., and during this period it was occasionally found necessary to cut off the current for intervals of a few minutes.

The last 5 per cent. (or less) was removed from the sweater as in the experiments [3] with oil-free wax. Difficulty was also experienced in this series of experiments in maintaining the desired rate of sweating during the fractionation of the last 10 per cent.

The sweats were collected, in general, in cuts of 5 per cent. by weight, and the melting point of each fraction of melting point higher than 100° F. was determined in the manner previously described. The melting points of fractions lower than 100° F. were not determined accurately, as the melting point method developed for this work, like the I.P.T. and A.S.T.M. methods, is not satisfactory for mixtures of oil and wax containing large amounts (greater than 50 per cent.) of oil. A rough determination was made in some instances, but a knowledge of these low melting points was not considered essential for this investigation. The refractive index at 60° C. was also found for each fraction, using the Abbé Refractometer.

In this series of experiments, as in those with oil-free wax, it is necessary to know the melting point and yield of wax, or oil–wax mixture, present in the sweater at any stage of the experiment. The fractions were therefore blended as before—starting with the last two collected—and the melting point, and also the refractive index at 60° C., found after the addition of each two consecutive fractions. Owing to the presence of oil, the relationship[1] $T = \frac{414{\cdot}5M}{94{\cdot}5 + M}$ cannot be applied to the calculation of melting points, except for those fractions collected after the removal of all the oil.

It was found that the presence of oil rendered the sweating much easier to control than in the experiments with oil-free wax. Little difficulty was experienced in reducing the temperature gradient in the wax–oil mass to 1° F., even in the stock containing only 2 per cent. oil.

This observation is of importance, as it is probable that any difficulties experienced with the laboratory sweater would be increased with industrial plant. It is possible that the presence of oil modifies the crystal structure of the wax in such a manner that sweating is facilitated. Other possible explanations may, however, be suggested. For example, if the surface tension between solid and liquid wax is greater than that between solid wax and oil and if the viscosity of the oil is lower than that of the liquid wax, the oil would flow more easily through the channels that are formed in the wax mass. Some evidence for the existence of these channels was found during the preparation of an oil–wax sample for one of the sweating experiments. The molten wax had been weighed into a beaker and had been cooled to a semi-solid state, such that when the oil was poured on to its surface it did not immediately percolate through. After standing for 1 hour, however, the oil had passed through the mass, leaving the top surface with a honeycomb structure. This observation suggests that sweating may take place through capillary action and that these capillaries or channels are more easily formed when oil is present.

Owing to the large difference between the refractive indices of the dewaxed Second Cooled Blue Oil ($n_D^{60} = 1{\cdot}4867$) and the various waxes obtained in the experiments ($n_D^{60} = 1{\cdot}4327 - 1{\cdot}4372$), the value of n_D^{60} for a wax–oil blend gives an indication of the oil content. The refractive indices of various blends of the dewaxed Second Cooled Blue Oil and the wax stock of melting point 122·1° F. are given in Table II.

TABLE II.

Wax, Weight %.	Oil, Weight %.	n_D^{60}
100	0	1·4342
98	2	1·4350
95	5	1·4367
90	10	1·4386
80	20	1·4434
70	30	1·4486
60	40	1·4536
50	50	1·4589
30	70	1·4696
0	100	1·4867

A graph of oil content/n_D^{60}, covering the range 0–50 per cent. oil, is linear. This linear relationship was used as a means of ascertaining the approximate oil content of this series of experiments.

It was found that the refractive index of the material (wax–oil) remaining in the sweater decreased during the removal of the first fractions, reached a minimum value, and then increased. The percentage of the material (wax–oil) in the sweater at the stage corresponding with the minimum value of the refractive index is given for each run in Table III.

TABLE III.

Run No.	20.	16.	12.	13.	14.	15.
Oil content of stock, % .	2	5	10	20	30	40
Minimum n_D^{60} . . .	1·4346	1·4344	1·4347	1·4351	1·4358	1·4366
Stock in sweater, % .	70	60/65	50	40	25	5

The position of the minimum refractive index corresponds to the stage at which the removal of the oil is almost complete, and it is seen from Table III above that the yields of nearly oil-free wax, independent of melting point, that may be obtained from the oil–wax mixture, depend on the original oil content of the latter.

The stage at which the oil has been almost completely removed from the stock is indicated in Fig. 1, in which the melting point is plotted against the refractive index at 60° C. for each of the single liquid phase fractions of melting point higher than 100° F. obtained in runs 12–16 and 20. The corresponding graph for the fractions obtained when using oil-free wax stock (Run 8) is also shown. The curve for each run approaches this latter curve as the melting point of the fraction increases, until a stage is reached at which the two curves meet and then become almost coincident. It is suggested that the two curves meet in each instance at the stage where the oil content of the wax present in the sweater is somewhat less than 1 per cent.

This figure of 1 per cent. was estimated as follows. It has been shown in Table II that the addition of 1 per cent. dewaxed Second Cooled Blue Oil to a wax of melting point 122·1° F. increases the refractive index of the latter by approximately 0·0005. It will be appreciated that the melting points of the waxes under consideration are higher than 122·1° F., but the error introduced by applying this linear relationship to such higher melting waxes is probably negligible, in view of the small difference in the refractive indices of waxes of melting points 120° F. and 140° F., compared with the refractive index of the oil. It was therefore assumed that the addition of 1 per cent. oil increases the refractive index of wax of melting point within this range by approximately 0·0005, an amount which could easily be detected with the Abbé Refractometer. It is seen from Fig. I that the curve for the fractions of corresponding melting points collected after the stage at which the curve for the run meets that for the oil-free stock (Run No. 8) does not deviate from the latter by more than 0·0002 in refractive index. It may therefore be concluded that the oil contents of fractions in this region are probably less than 1 per cent. It is of interest to note from Fig. 1 that the curve for the wax stock originally containing 40 per cent. oil approaches, but does not meet, the curve for the oil-free stock (Run No. 8). It is therefore to be inferred that, under the particular conditions of sweating employed in this investigation, it is not possible to obtain a substantially oil-free wax from stocks containing 40 per cent. or more oil.

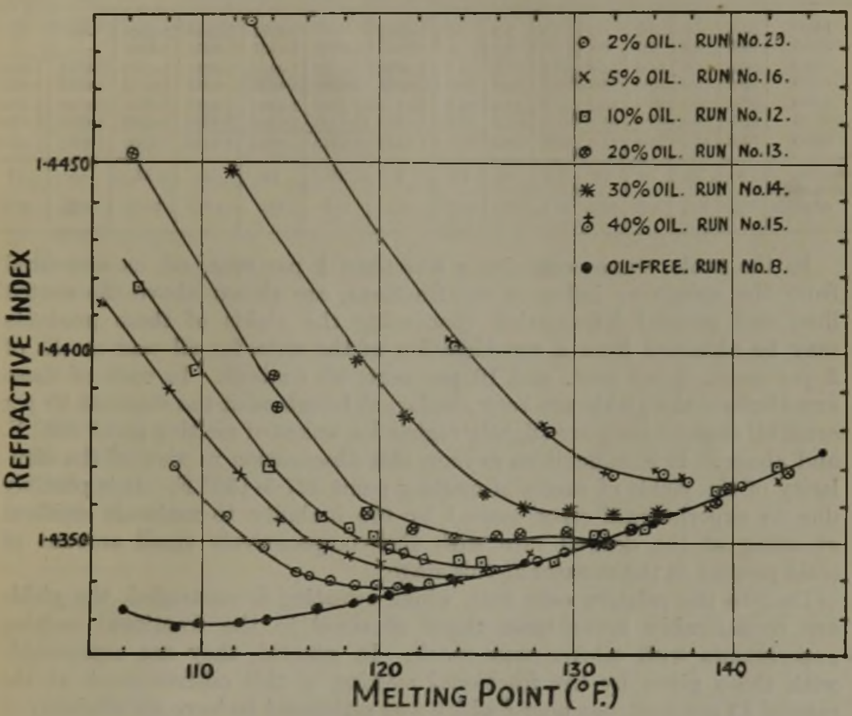

FIG. 1.

Yield, melting point, and refractive index data are given in Table IV for waxes of various melting points higher than 125° F., the yields being expressed as a percentage of the total wax present in the original wax–oil stock. The yields and refractive indices of the corresponding waxes obtained from oil-free wax (Run No. 8) are also included. The refractive indices for the blended fractions in the run were calculated from those of the single fractions assuming refractive index to be additive over the small melting point range involved.

TABLE IV.

Melting point, ° F.	Yield, per cent. by weight. Calculated as per cent. of wax present in the wax-oil stock.							Refractive index at 60° C. (n_D^{60}).						
140·0	10·4	—	3·2	3·0	3·0	3·3	—	1·4367	—	1·4367	1·4366	1·4368	—	—
137·5	16·5	5·3	6·7	8·1	7·7	8·9	—	1·4362	1·4362	1·4361	1·4361	1·4361	—	—
135·0	24·2	13·0	14·3	14·8	13·4	12·1	10·1	1·4357	1·4357	1·4356	1·4357	1·4357	1·4361	1·4366
132·5	34·4	23·5	25·3	23·9	25·2	26·0	25·8	1·4352	1·4352	1·4351	1·4352	1·4353	1·4358	1·4369
130·0	47·0	36·7	38·4	37·2	43·7	43·4	36·3	1·4347	1·4348	1·4347	1·4348	1·4351	1·4358	1·4383
127·5	61·5	53·4	53·9	54·7	61·2	57·7	44·2	1·4345	1·4346	1·4346	1·4347	1·4353	1·4368	1·4398
125·0	78·8	74·7	73·2	74·6	75·2	68·9	52·2	1·4342	1·4345	1·4345	1·4349	1·4362	1·4383	1·4412
Run No. .	8	20	16	12	13	14	15	8	20	16	12	13	14	15
Oil content of stock	0%	2%	5%	10%	20%	30%	40%	0%	2%	5%	10%	20%	30%	40%

In the table, waxes containing less than 1 per cent. oil, as estimated from the refractive index of the fractions, are shown above the dotted line, and general information concerning the yields of these products may be obtained from a consideration of the data for oil–wax stocks of 2 per cent., 5 per cent. and 10 per cent. oil content. In each of these experiments the yields are very similar, although with the stock of 10 per cent. oil content they are slightly higher for waxes of melting point 135° F. and above. It is difficult to explain this observation in view of the similarity of the yields of waxes of melting point 127·5–135° F. It is possibly due to experimental error caused by the inability to maintain uniform sweating at the desired rate with the comparatively small amount of solid present in the sweater at this stage.

Despite the relative ease with which sweating is controlled, the yields are considerably lower than those obtained in the fractional melting experiments with oil-free wax stock. In general, they are comparable with those given by the fractional melting of this oil-free stock at the rate of 15 per cent. per hour,[3] which was estimated to have an efficiency of 78 per cent. compared with the assumed 100 per cent. efficiency of Run No. 8. Fractional melting at the rate of 5 per cent. per hour was estimated on the same basis to be 90 per cent. efficient. Otherwise expressed, the yields of substantially oil-free (less than 1 per cent.) waxes of melting point 127·5° F. and above, obtained from the wax–oil stock containing 2–10 per cent. oil, are in the region of 10–12 per cent. lower than those of corresponding melting point obtained under the same conditions by the fractional melting of the oil-free wax stock.

It is apparent that for products of melting point 127·5° F. and above the addition of 2 per cent. oil to the oil-free wax stock has much the same effect as 10 per cent. For products of lower melting point there is a difference, however, for their oil contents vary with the amount of oil initially present in the wax stock.

In view of the comparatively poor yields of lower-melting-point wax obtained from the oil–wax stock of 40 per cent. oil content, and also the failure to obtain a substantially oil-free wax of any melting point from this stock, it is suggested that an oil content of 40 per cent. is above the maximum for satisfactory sweating.

Assuming that one of the objects of sweating is to produce a substantially oil-free scale wax of melting point at least 127·5° F., there seems to be no advantage gained by reducing the oil content of the stock below 10 per cent. Also, as the yield of this oil-free product from a stock containing 20 per cent. oil is relatively much lower than from one containing 10 per cent. oil, it is concluded that for satisfactory and efficient sweating the oil content of the stock should be reduced to 10–12 per cent. by weight.

Effect of Rate of Sweating.

As the effect of the sweating rate variable has already been investigated and discussed in a previous publication for the case of oil-free wax, it was felt that for the present case of oil–wax mixtures this would be sufficiently examined by two runs with oil–wax mixtures containing 10 per cent. of oil, at sweating rates 5 per cent. and 10 per cent. per hour.

Run No. 12 supplied all the necessary data at the 5 per cent. per hour rate, and a new run, No. 21, was carried out at the 10 per cent. per hour rate.

The wax-oil sample containing 10 per cent. oil was prepared in the normal manner, cooling taking place at room temperature overnight. The temperature gradient in the wax–oil mass during sweating could not be reduced below 2° F. Otherwise the experiment proceeded normally.

The yields and refractive indices of waxes of melting point higher than 125° F. remaining in the sweater at a given stage for these runs are given in Table V.

Table V.

Melting point, ° F.	Yield, Weight %.	n_D^{60}.	Yield, Weight %.	n_D^{60}.
140	2·7	1·4366	3·0	1·4367
137·5	7·3	1·4361	6·6	1·4363
135	13·3	1·4357	12·9	1·4359
132·5	21·5	1·4352	22·2	1·4356
130	33·5	1·4348	33·5	1·4353
127·5	49·2	1·4347	48·8	1·4352
125	67·2	1·4349	66·4	1·4356
Run No. . .	12		21	
Oil content of stock	10%		10%	
Rate . . .	5% per hour		10% per hour	

Inspection of the above figures shows that, within experimental error, the yields are the same in each run, although the waxes of melting point below 135° F. from the run at the faster rate are of slightly higher oil content than those of corresponding melting point from the slower run. As there is no doubt that the yield of wax of a given melting point obtained from an oil-free wax stock is dependent on the rate of fractional melting, the similarity of the yields obtained in the two experiments under consideration is therefore rather unexpected. It is possible, however, that sweating at a rate considerably slower than 5 per cent. per hour would lead to increased yields of the various waxes.

Effect of Method of Preparing Sample.

Two runs were made for the purpose of investigating the extent to which the efficiency of the process is affected by the way in which the wax–oil sample is prepared prior to sweating. Wax–oil mixtures containing 10 per cent. oil were used in these experiments.

Partial Cooling.

The sweater was prepared in the normal manner and the wax–oil sample introduced at a temperature of 130° F. Cooling took place in the absence of draughts until the central region of the mass was at a temperature of 87° F. At this stage a temperature gradient of 4° F. existed in the mass. The cellophane was removed from the outer surface of the sweater, and the latter placed inside the external heater, which had been heated so that the temparature of the air inside was 80–83° F. Sweating at the rate of 5 per cent. per hour was then conducted in the normal manner, the initial drops of liquid appearing in the collecting beaker after 10 minutes' heating.

Shock Cooling.

The sweater was prepared in the normal manner and the wax–oil sample introduced at a temperature of 135° F. The sweater and contents were immediately plunged into an acetone-solid CO_2 bath cooled to $-50°$ C. The bath temperature quickly rose to $-25°$ C. and was maintained at $-25°$ C. to $-30°$ C. for 1 hour whilst the wax–oil sample solidified. On removal from the cooling mixture, the central region of the mass was at a temperature of 55° F. The sample remained at room temperature overnight, and sweating at the rate of 5 per cent. per hour was commenced on the following day.

The sweating appeared to proceed normally in each instance.

The yields and refractive indices of various waxes of melting point higher than 125° F. remaining in the sweater at given stages are given for Runs 18 and 19 in Table VI. The corresponding figures for waxes obtained from the same stock at the same rate of sweating after preparation of the sample in the usual manner (Run No. 12) are included for comparative purposes.

It may be observed that the yields of waxes of the same melting point obtained in the three runs are not very different. There is, however, an indication that the yields of waxes of melting point 135° F. and above are slightly higher in the experiment involving normal cooling of the sample.

The slightly lower yields in the experiment involving partial cooling might possibly be attributed to the wax crystals not having been allowed sufficient time in which to attain the size of those formed during normal cooling to room temperature (Run No. 12).

Table VI.

Melting point, ° F.	Normal cooling.		Partial cooling.		Shock cooling.	
	Yield, Weight %.	n_{D}^{60}.	Yield, Weight %.	n_{D}^{60}.	Yield, Weight %.	n_{D}^{60}.
140	2·7	1·4366	—	—	—	—
137·5	7·3	1·4361	6·5	—	5·0	1·4364
135	13·3	1·4357	10·2	1·4360	12·0	1·4359
132·5	21·5	1·4352	20·4	1·4355	22·2	1·4355
130	33·5	1·4348	34·6	1·4352	34·9	1·4352
127·5	49·2	1·4347	50·5	1·4351	50·5	1·4353
125	67·2	1·4349	67·6	1·4353	66·7	1·4356
Run No.	12		18		19	
Oil content of stock	10%		10%		10%	
Rate	5% per hour		5% per hour		5% per hour	

Rapid or shock cooling would almost certainly cause the formation of very small crystals, especially in the region of the wax–oil mass near the surface of the sweater, where the cooling conditions are most severe.

The refractive index data indicate that the residual waxes of melting point 125° F. and higher, present in the sweater at any given stage in these two runs, contain slightly more oil than those of the same melting point obtained in Run No. 12. It may be inferred from this observation that partial, as well as shock, cooling of the wax–oil sample causes the formation of small wax crystals, which are of such a nature that oil is less easily removed from them during the process of sweating.

The variations in the yields and refractive indices are not, however, sufficiently great to allow any very detailed conclusions to be reached.

It is clear, however, that the rate and extent of cooling of the sample prior to sweating have little effect on the efficiency of the process.

Effect of Viscosity of the Oil.

Oils of different viscosity for use with the oil-free wax stock in a study of the effect of oil viscosity on the sweating process, may be obtained as follows :—

(i) the viscosity may be varied by employing various oils of different boiling ranges, or

(ii) the desired viscosity may be obtained by blending two dewaxed oils of high and low viscosity respectively.

The use of oils of different boiling ranges introduces complications due to the variation in chemical composition, and it was therefore decided to prepare oils of the desired viscosities from two stocks of dewaxed oils. This method ensures that the same constituents are present in each blend, although, of course, in different proportions.

Oil Stocks.

The dewaxed Second Cooled Blue Oil, used in the previous experiments, constituted the stock of low viscosity.

The high-viscosity stock was prepared from a Master Lubricant oil supplied from the Anglo-Iranian Oil Co.'s Llandarcy Refinery.

The Second Cooled Blue Oil is obtained from the crude by cold pressing the light wax distillate, and the Master Lubricant is a dewaxed heavier distillate taken from the crude immediately following the light distillate. This heavier distillate was dewaxed on the refinery, using the Sharples process, but it was further dewaxed in the laboratory with ethylene dichloride at −25° F. by the method already described for the Blue Oil. The laboratory dewaxing resulted in a very sticky or resinous oil having the following properties :—

Specific gravity at 60° F.	1·010
Pour point	20° F.
n_D^{60}	1·5587
Viscosity :	
Redwood II at 100° F.	4323 secs.
Redwood II at 140° F.	438·6 secs.

Blends covering a considerable viscosity range could therefore be prepared from these two stocks, and it was proposed to investigate the effect of oils over the complete viscosity range. However, the scheme was interrupted after completion of only two runs, the results of which are now discussed.

In view of the findings in the experiments with oil–wax stocks, it was decided to employ stocks of 10 per cent. oil content. In each instance the sample was prepared in the normal manner, and sweating was conducted at the rate of 5 per cent. per hour. No difficulty was encountered with either stock.

The yields and refractive indices of various waxes of melting point higher than 125° F. remaining in the sweater at given stages are recorded in Table VII. For purposes of comparison, the corresponding figures for Run No. 12 are included.

TABLE VII.

Melting point, ° F.	10% D.B.O.		9% D.B.O. + 1% D.M.L.		7% D.B.O. + 3% D.M.L.	
	Yield, Weight %.	n_D^{60}.	Yield, Weight %.	n_D^{60}.	Yield, Weight %.	n_D^{60}.
140	2·7	1·4366	5·0	1·4368	3·5	1·4369
137·5	7·3	1·4361	10·0	1·4364	7·8	1·4365
135	13·3	1·4357	16·4	1·4359	13·8	1·4361
132·5	21·5	1·4352	25·5	1·4355	23·2	1·4356
130	33·5	1·4348	37·2	1·4353	34·6	1·4353
127·5	49·2	1·4347	52·2	1·4353	47·8	1·4354
125	67·2	1·4349	67·0	1·4355	63·7	1·4357
Run No.	12		22		23	
Rate	5% per hour		5% per hour		5% per hour	

D.B.O. = Dewaxed Blue Oil.
D.M.L. = Dewaxed Master Lubricant.

The experimental data are insufficient for any general conclusions to be stated relating to the effect of the viscosity of the oil on the efficiency of the sweating process. However, the minimum values of n_D^{60} for Runs 22 and 23 are higher than for Run 12 and, moreover, correspond with a higher percentage of residual wax (wax–oil) in the sweater than for Run 12. These observations indicate that the oil of higher viscosity is more difficult to remove from the wax.

In addition to the above experiments with oils of different viscosities, a run was made with a wax–oil mixture consisting of :—

> 70 per cent. oil-free wax, 15 per cent. D.B.O. and 15 per cent. kerosine (sp. gr. at 60° F. = 0·8025).

The sample was prepared in the usual manner, and sweating was carried out without difficulty at the rate of 5 per cent. per hour.

The comparison of the yields of various waxes obtained in this run with those obtained in Run No. 14, in which the oil–wax stock contained 30 per cent. Dewaxed Blue Oil, is given in Table VIII.

TABLE VIII.

Melting point, ° F.	Yield.	Per cent. by weight.
140	2·4	—
137·5	6·2	—
135	8·5	4·8
132·5	18·2	18·6
130	30·4	28·2
127·5	40·4	35·2
125	48·2	39·8
Run No. . . .	14	17
Oil content of stock .	30% D.B.O.	15% D.B.O. 15% Kerosine

The results of this run are included in order to mention the significance of the comparatively low yields of waxes of melting points 125° and 127·5° F. obtained.

These low yields may be attributed to the higher solubility of the wax in the Blue Oil–Kerosine blend than in the Blue Oil alone. It is therefore suggested that any study of the effect of viscosity should be made in conjunction with experiments on the solubility relationships of the wax and the various oil blends employed.

CONCLUSIONS.

(1) The sweating of an oil–wax mixture is considerably easier to control than the fractional melting of an oil-free wax. This is of particular importance industrially, as ease of control of a process, especially on the commercial scale, is very desirable.

(2) The yields of the various melting-point waxes, calculated as a percentage of the wax content of the oil–wax stock, are considerably

lower than for the corresponding waxes obtained by the fractional melting of the oil-free wax stock at the same rate.

(3) Under the same conditions of sweating, the efficiency of the process is dependent on the oil content of the stock. Little or no advantage is to be gained by de-oiling the stock to an oil content of less than 10 per cent. Also, the most satisfactory sweating stock contains 10–12 per cent. oil. At the other extreme, it is evident that an oil content of 40 per cent. is above the maximum for efficient and satisfactory sweating.

It will be appreciated, however, that these deductions are based on the results of experiments conducted at the same rate of sweating. It is possible, therefore, that a stock containing 40 per cent. oil could be satisfactorily processed at a considerably slower rate, especially during the collection of the first few fractions, when the loss of wax—due to solubility in the oil—would be reduced.

(4) The rate and extent of cooling of the sample prior to sweating have little effect on the yield and oil content of the various waxes produced.

(5) For corresponding melting points, the yields of waxes obtained by sweating at 5 per cent. and 10 per cent. per hour are similar, but those from the faster process are of slightly higher oil content. It is probable that a higher efficiency would result from sweating at a rate slower than 5 per cent. per hour, especially in the initial stages, when the oil content of the stock is comparatively high.

(6) The effect of viscosity has not been studied in detail, but in the limited experimental work performed on this factor results have been obtained which indicate that oil of higher viscosity is more difficult to remove from the wax, and the resulting wax is therefore of higher oil content.

No experiments were made to ascertain the effect of over-heating in the wax–oil mass, as it is clear from the experiments with oil-free wax that strict control and regulation of the temperature throughout the mass is essential for satisfactory sweating.

References.

[1] Sawyer, Hunter and Nash, *J. Instn Petrol.*, 1940, **26**, 390.
[2] *Idem, ibid.*, 1940, **26**, 430.
[3] *Idem, ibid.*, 1941, **27**, 1.

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OBITUARY.

CARLETON ELLIS.

Carleton Ellis, who was a Fellow of the Institute, died in Miami Beach, Florida, on 13th January last, influenza being the immediate cause of his death. He was born in Keene, New Hampshire, U.S.A., on 20th September, 1876, and received his early training as a chemist at the Massachusetts Institute of Technology, where the degree of Bachelor of Science was conferred upon him in 1900, and where he taught for two years following.

Whilst at this Institute the inventive genius of Carleton Ellis commenced to assert itself, but, as is the experience of most technical men, he early discovered that whilst an original idea might be developed by hard work, patience, and initiative, to turn it to economic value required also hard cash, which went mostly into the pockets of patent agents. He therefore commenced a study of patent law, and in time received a certificate qualifying him to practice before the Patent Office of the United States.

The work of this great industrial scientist was spread over a wide range of organic chemistry, for Carleton Ellis had worked extensively in the field of edible oils, fats, waxes, synthetic resins, paints, varnishes, petroleum products, and gasoline manufacture, and for some years he had governed the Ellis Laboratories at Montclair, New Jersey. In addition to this, he had acted as Consultant on the Technical Committee and Chemical Committee of the Standard Oil Company of New Jersey for a considerable period.

During his career, Carleton Ellis was responsible for more than 700 patents, a record exceeded in the U.S. Patent Office by only two other scientists, Thomas A. Edison and a John O'Connor. The work for which he was best known was in connection with catalytic hydrogenation, petroleum oxidation, chemical derivatives from petroleum, the production of alcohols from still gases, synthetic resins and plastics, and nitrocellulose and analogous derivatives of cellulose.

The results of his researches and studies were presented in the form of such monumental works of reference as : " The Hydrogenation of Organic Substances," " The Chemistry of Synthetic Resins," " The Chemistry of Petroleum Derivatives," " The Chemical Action of Ultra-violet Rays " (considered by a Committee of the League of Nations as one of the most important scientific books of 1925), as well as in numerous papers published in technical journals. As an example of his catholicity, reference might be made to two discoveries for which he was responsible. The first was the finding of a profitable market for the milk recovered from the udders of slaughtered cows. His solution was a dog biscuit made in the shape of a bone, which soon had a ready sale. The other was another of his earlier commercial successes, the development of the Tube and Tank method of cracking heavy petroleum products, which then had a limited use.

Carleton Ellis was a past president of the New Jersey Chemical Society, a member of the American Chemical Society and of the American Institute of Chemical Engineers, a Fellow of the Chemical Society, and Edward Longstreth medallist of the Franklin Institute. As can be imagined, he was a voracious reader, but, despite his busy life, he found time to devote a certain period every year to travel, in order to meet old friends and, due to his charming personality, he invariably made many new friendships on these occasions.

Some years ago Carleton Ellis spent a short time in the petroleum laboratories at the University of Birmingham, England, when the writer formed a happy and lasting friendship with him : it was soon evident that he possessed the ability of inspiring confidence and the team spirit in his juniors, and of drawing the best from them by his natural pleasing manner and power of leadership.

At the last World Petroleum Congress, members of this Institute had the pleasure of meeting both Carleton Ellis and his charming wife.

To his relatives we extend our deepest sympathy.

A. W. Nash.

JOHN ARTHUR CARPENTER.

John Arthur Carpenter, M.A., F.I.C., a Devonian by birth, was educated at Exeter School. At New College, Oxford, he took First Class Honours in Mathematical "Mods." and Chemical Finals, and later a Second Class in Physics. He was President of the Oxford University Junior Scientific Club, Demonstrator in Chemistry at Christ Church, and Lecturer and Tutor in Physics at University College, Exeter. Subsequently he was a Master in St. Paul's School, London.

He served in the Great War of 1914–18, retiring with the rank of Major.

In 1922 he became Research Chemist in charge of the Experimental Laboratory of the Syriam Refinery of the Burmah Oil Co., Ltd., in which capacity he remained until his sudden death on December 2, 1940.

Carpenter, who became a Member of the Institute in 1925, contributed some useful papers to the *Journal*, including :

"The Physical and Chemical Properties of Paraffin Wax, particularly in the Solid State" (1926, **12**, 288).

"The Composition of Petroleum (Kerosine and other) Fractions, with a Standardization of Miscibility and Optical Tests" (1926, **12**, 518).

(With J. P. Fraser) "Regulation of Velocity of Flow of Fixed Quantities of Liquid over Surfaces" (1927, **13**, 725).

"The Composition of Petroleum (Kerosine and other) Fractions" (1928, **14**, 446).

W. J. Wilson.

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.

339.* Hawkins Field Rated Largest Reserve Added in Year. B. Mills. *Oil Wkly*, 3.2.41, **100** (9), 12.—The Hawkins producing area appears to cover 7500–10,000 acres, with 25–200 ft. of oil-sand in the Woodbine. Its reserve is estimated at 300–600 million brl. The structure is an elongated anticline with closure of about 450 ft. The maximum thickness of Woodbine sand is about 700 ft., of which the upper 100–150 ft. may carry gas. This structure arises from thinning of the interval between the Pecan Gap chalk and the Woodbine sand. The porosity of the producing sand is about 25%, and its permeability is high. In some parts there are shale-breaks in the oil-zone. A heavy gas-flow was encountered in the Eagle Ford overlying the Woodbine. It is possible that the structure is faulted. Brief details of the logs of the few wells are given, and the indications are that the wells will average 4600–4900 ft. in depth.

Hawkins was outlined by surface, subsurface, and geophysical data, but the producing limits are not yet fully defined.

Brief details of the drilling procedure are given. The formation pressure is 2200 lb./in.^{2} Two electrical logs of the formations are appended. G. D. H.

340.* Better Concept of Faulting Patterns Aids Piercement-Dome Development. M. M. Kornfeld. *Oil Wkly*, 10.2.41, **100** (10), 19.—Faults may dislocate cap-rock and flank production around salt domes so much as to make ordinary means of exploration so hazardous as to require excessive uneconomic drilling to find production. Now experimental master-fault systems can be superimposed on salt-dome maps to help in locating fault-zones which would ordinarily be discovered only by drilling. Experiment shows that there are peripheral and radial faults, and their presence has been demonstrated on piercement salt-domes. The radial faults may be variable, but the pentagonal plan seems to dominate. Peripheral faulting leads to barren zones between the cap-rock and flank producing areas. The experimental work has indicated lines of attack which are superior to the old trial-and-error methods. A knowledge of salt-dome fault patterns assists in the interpretation of soil surveys.

On the Gulf Coast flank production may come from the Frio, Vicksburg, Jackson, Cockfield, Yegua, and Cook Mountain. Deep-seated salt-domes have given oil from the Mount Selman and Wilcox. G. D. H.

341.* Well Completions this Year Run Below 1940 Curve. L. J. Logan. *Oil Wkly*, 10.2.41, **100** (10), 33.—Although drilling activity fell early this year, it may rise later. The war is partly responsible for the fall, which may be partly offset by the rise in drilling which will undoubtedly take place as a result of increased industrial and commercial activity.

In 1939 and 1940 there were increases in the average output per well, those averages being 9·1 and 9·2 brl./well, respectively. The output per well in 1939 and 1940 rose in Arkansas, Illinois, Indiana, Kansas, Mississippi, Montana, Nebraska, and Wyoming, but it fell in California, New Mexico, Oklahoma, and Texas.

Drilling in January 1941 in U.S.A. was 13% below the level of drilling in January 1940. Tables give the completions by States for January and December 1940 and for January 1941, and the types of completions are listed. The drilling activity at the beginning of January 1940 is compared with that on 1st January and 1st February, 1941. G. D. H.

342.* Northern Hemisphere Offers Greater Oil Possibilities. W. V. Howard. *Oil Gas J.*, 9.1.41, **39** (35), 14; 6.2.41, **39** (39), 16.—Geologically and geographically the world's oil production can be divided into three nearly equal parts—Tertiary production in North America, Tertiary production in the rest of the world, and Mesozoic and Palæozoic production in North America. From a geological point of view the world can be considered as having northern and southern hemispheres which have similar elements—namely, three large and some smaller shields of pre-Cambrian and other metamorphics, surrounded by relatively undisturbed sediments and elongated arcuate chains of folded rocks, but in detail there are differences which bear on the possibilities of finding oil, especially in the Palæozoic and Mesozoic.

The southern hemisphere has five fragments of a former continent, but much of it has been submerged for only relatively short periods. In the late Palæozoic it was extensively glaciated, the glacial deposits burying the older rocks and being succeeded by a great thickness of continental beds. These mask almost all pre-Pennsylvanian structures and reduce the effectiveness of geophysical work. This continent began to split up in Triassic times, and later there were extensive outpourings of basaltic lava. Sedimentaries were laid down in the Amazon valley area and North Africa, making possibilities of oil like those of Wyoming. Hence, practically only the margins of the fragments of the southern continent have good oil possibilities. Gently folded Mesozoic and Tertiary beds and some wedges occur (*e.g.*, Egypt, Argentine). It is in the great folded belts of the north and west of this former southern continent that most of the oil of the southern hemisphere is found.

The northern hemisphere had no Palæozoic glaciation, and the Pleistocene glaciation was not extensive in possible oil regions. The Hercynian folding added much to the northern continent, and there were many opportunities for oil formation and accumulation. Thus multiple oil-plays were formed in North America. Palæozoic flysch areas occurred in North America, south-west of Fenno-Scandia, the Russian platform, and Western Siberia. Hence Russia has two areas potentially like the mid-Continent region of North America.

In addition to oil in flysch deposits, it is found in more extensive limestones and sandstones which give oil on broad regional features. In the mid-Continent, Russia, and West Siberia such deposits from shallow extensive seas were laid down.

Mesozoic and Tertiary sea invasions took place in Wyoming and Montana, and Germany's fields are of this type, as are also those of the Emba region and Turkestan. A Mesozoic sea invasion from the south was extensive only in U.S.A.

The Andine Revolution, which culminated in the Cretaceous, affected a belt from Antarctica to Alaska. Oil accumulations are associated with it in various parts of North and South America. It swings south through Japan and Borneo, where some oil has been found, but these regions are far from fully tested. Much of the length of the Alpine chains lies on highly folded Palæozoic, with the consequent minor oil possibilities, but in the open-folded flysch areas prospects are better. There are better oil chances in the southern ranges of this system—Iraq, Iran, Burma, East Indies, etc. The structure and deposits of the Gulf Coast of Texas and Louisiana are almost unique.

The various oil-field types are tabulated with examples, and a number of diagrams are included. G. D. H.

343.* Well Logs and Field Data of Active Oil Areas—Southern Mississippi. Anon. *Oil Gas J.*, 6.2.41, **39** (39), 42.—Before the discovery of Tinsley in 1939 the only Mississippi production was from the Jackson and Amory gas-fields. Ninety-six wildcats were drilled in 1940. Tinsley produces from five sands in the Selma, Eutaw, and Tuscaloosa of the Upper Cretaceous. At Pickens production is from the Wilburn sand of the Eutaw.

The principal structural trend is a continuation of the Cincinnati–Nashville arch. The Tinsley dome is an uplift on the north-east flank of this major structure. In the southern part of the State are east–west structures, of which the Hatchetigbee anticline is the chief. More than 150 wildcats have been drilled in Mississippi, but many were poorly located with regard to structure or were not drilled sufficiently deep. South of the Yazoo county fields the Eocene–Wilcox would appear to have as good possibilities as in the west. Drilling around the salt-domes has not yet been successful. Palæozoic rocks in Mississippi are known to be asphaltic at outcrop, especially in the Mississippian. Thus they may yield oil at depth. Amory gave gas from the Hartselle sandstone (Mississippian). One of the difficulties has been that of interpreting geophysical data satisfactorily. The Tinsley reserves are estimated at 37,000,000 brl.

A geological map, stratigraphical column, and a series of well sections are included.
G. D. H.

344.* Importance of Two California Discoveries Yet Undetermined. L. P. Stockman. *Oil Gas J.*, 13.2.41, **39** (40), 26.—A 100-brl. well was completed recently in the Union Avenue district of Kern Co. It was brought in in the Santa Margarita at 5275–5315 ft. The Pliocene Kern River and Chanac series were barren. A well in this area had previously been taken to 10,427 ft. without success. A 100-brl. well was also brought in in the Newhall district of Los Angeles Co. It is on the Hasley anticline of the Newhall–Castiac region, and gives oil from the Modelo at about 2415 ft., a much less depth than was expected. Both areas need further testing before their potentialities can be assessed.
G. D. H.

345.* Air Photography and Geology.—R. W. Willett. *N.Z.J. Sci. and Tech.*, July 1940, **22** (1B), 21 (B).—The development of the use of air photographs as an aid to geological work in New Zealand is described and a detailed discussion is given of the difficulties, results, and possibilities of interpretation of geological features from air photographs. Air photographs in oil geology have given a great impetus to interpretative technique and hold to-day a recognized place in the mapping of petroleum-bearing areas. The delineation of anticlines, synclines, faults, dips, strikes, etc., are discussed in detail. A section is devoted to the relative costs of air-photographic and ground-survey work. A good bibliography is appended.
B. M. H. T.

Drilling.

346.* Selection of Wire Rope for Rotary Drilling Lines. H. F. Simons. *Oil Gas J.*, 23.1.41, **39** (37), 32–34.—As far as the rotary-drilling industry is concerned there are two types of wire lines used. One is the 6-by-19 Seale-type, regular right-lay, round-strand construction, and the other is the 6-by-19 Seale, Lang-lay, flattened-strand construction; the latter is generally furnished preformed. The 6-by-19 Seale-type wire line has six strands, each strand of which consists of a core wire surrounded by nine inner wires of uniform but relatively small size, and on the outside by nine wires of uniform but relatively larger size. Variations of this type-line (used elsewhere than in the oil industry) may have a different number of wires than nine, but the principle of construction remains the same.

The term " Seale " means that there are two layers of interlocking wire, the outer layer set in the valleys of the layer beneath. For ropes of the same diameter the outer wires of a Seale-constructed rope are larger components of the strand, and thus offer more resistance to abrasion. High resistance to abrasion is particularly important in the drilling industry.

The lay of ropes is discussed, and the regular lay is compared with the Lang-lay for drilling purposes. Grades and materials used are studied together with ultimate strengths. The paper is the first of a series, and deals mainly with the manufacturing side of wire ropes.

A table gives the sizes of lines for different jobs, and formulæ enable one to calculate block efficiency of line systems.
A. H. N.

347.* Rotation of Casing while Cementing. H. F. Simons. *Oil Gas J.*, 23.1.41, **39** (37), 50.—A method of rotating casing while cementing is described. After the casing has reached bottom and circulation has been established, rotation of the casing is started. The cement is mixed and pumped into the pipe with the weight of the slurry kept between 15·6 and 15·7 lb./gal. As soon as the cement has been pumped into the pipe, the regular plug is placed in casing and displacement begun with mud, a weighted measuring line following the plug to check its position and the position of the cement. Rotation of the casing is maintained to ensure the even distribution of the cement.

From 25 to 30 r.p.m. of the casing has been used in the Cumberland field during the time the cement was being displaced. The time required for this is generally about

15 min., although the time varies, depending on the fluid capacity of the pump and the horse-power of the driving end.

The tool used for supporting the casing while rotating has a tool-joint box for screwing on to the swivel on one end, and a becket and pin, which is placed through the single-ball elevators. It has no name, although some call it a " circulating hood." The tool-joint box has an A.P.I. left-hand thread to match the pin on the swivel. This special tool has a 2-in. connection to which a flexible steel hose is attached for conducting the mud and cement from the swivel to the regular cementing head. Elevator bails, hose, and casing all rotate together. The drive is through the rotary table by means of clamps. A. H. N.

348.* Factors Affecting Wear of Rotary Drilling Lines. H. F. Simons. *Oil Gas J.*, 6.2.41, **39** (39), 34–35.—During the past 10 years the footage drilled with one change of rotary drilling lines has more than doubled, due to the improvement in the quality of the wire rope, increase in the rate of penetration and weight carried on the bit, better-designed and more appropriate drum and sheave sizes, and a wider knowledge of the proper installation and care of this particular piece of machinery.

There are several points where the wear on the line in the derrick and through the blocks is concentrated. The first of these is at the drum when the travelling block is: (*a*) as close to the floor as it gets while pulling or running-in drill-pipe ; (*b*) as close to the crown-block as it gets while making a trip ; (*c*) about 40 ft. off the floor, the position it is in when breaking out or adding a joint of pipe. The second main point of wear is at the crown-block when the travelling block is in each of the three positions listed above. A third is at the fast sheave on the travelling block in each of the same positions. It is possible to observe these facts and to minimize their effects by changing the position of the drilling line.

Factors affecting the wear on wire rope, such as diameter and grooves of sheaves, diameter of drum, lubrication, and fleet angle, are discussed. All these must be within certain limits to give minimum wear. A. H. N.

349.* Unusual Conditions in Deep Coastal Wells Present Completion Problems. N. Williams. *Oil Gas J.*, 13.2.41, **39** (40), 42–44.—In several Gulf-Coast fields in which development of productive sands at depths below 11,000 ft. has been undertaken within recent months, control and completion of wells have presented a number of new problems. Not only have high pressures been encountered, but high temperatures, hot salt-water flows, and excessive sand conditions have added to the difficulties of maintaining properly conditioned drilling mud to combat the pressures. Completion of wells at these depths has been complicated by the use of heavier muds which have been made necessary by the high pressure and unusual conditions which have had to be overcome.

Detailed drilling and control practices are given for typically difficult cases. Mud control is of the utmost importance in these fields. Three distinct means are employed in determining any change in mud and mud weights due to presence of gas or other conditions. First, there is the mud analyser, or hydrocarbon detector. Second, a continuous recording mud-weight indicator is provided. The third is to keep a close gauge of the amount of mud in the pits, the height of the mud in the pits being a ready indication of gas or other changes in mud condition.

Successful completion practices under difficult conditions are described.

A. H. N.

350.* Installation of Wire Rope used for Rotary Drilling Lines. H. F. Simons. *Oil Gas J.*, 20.2.41, **39** (41), 53.—A great amount of damage is often done to the wire rope while it is being installed on a rotary and drilling rig, and proper handling during this procedure will result in added service. Kinks in the line should be prevented at all costs, and the line should be spooled evenly and smoothly on the drum.

General practice is to jack up the reel, using as large a piece of pipe as possible through the centre of the reel for an axle. The free end of the rope can then be pulled to the derrick. After laying down the blocks, the free end of the new line is fastened to the dead end of the old line, and, by winding the old line on the drum, the new line is threaded through the blocks. If a guide-pulley is needed on the derrick floor it should be large enough to prevent kinking of the strands in the wire rope; a tubing block is excellent for this purpose.

The first layer of wire rope should be spooled on the drum tightly. This can be accomplished by putting a brake or weight on the reel, by attaching the cat-line to the fast line just under the crown-block, and then holding a strain on the cat-line as the line is wound on the drum, or by fastening a manila rope about 40 ft. up in the derrick and taking eight or ten wraps around the line; a tension on the free end of the manila rope automatically tightens its grip on the wire line. To prevent bending of the girts a bridle may be swung from the derrick legs for attachment of this tightening line.

Similarly other detailed procedures for safely installing wire ropes are given and illustrated. A. H. N.

351.* Occurrence and Treatment of Heaving Shale. Anon. *Oil Gas J.*, 27.2.41, **39** (42), 76.—No widely accepted explanation of the cause of heaving amongst certain shales is known. Instances are reported where the heaving shale cores have literally exploded on the derrick floor on removal from the core barrel. It is widely recognized that the presence of bentonitic material in the shale (which has the well-known property of expanding when saturated with water) is a contributing factor in the heaving action, but other conditions must coexist. In Wyoming, for example, the highly swelling bentonite does not cause heaving difficulties. It is possible that a steep angle of repose of the bentonitic stratum may be the coexisting condition necessary to start slipping and consequent plastic flow.

As bentonite is so important in these studies, a method of identifying montmorillonite, its most common component, is given. Benzidine is slightly soluble in water (about 0·5%); hence a saturated solution is readily prepared by shaking the benzidine with water. This, when packed in a small bottle, is the reagent. A small white test-plate, dropper, and penknife complete the equipment. When a sample of clay is to be tested, a small amount of dry clay is placed on the test-plate; a few drops of the benzidine reagent are used to wet it, and if a vivid blue colour results, montmorillonite is probably present. The test is sufficiently sensitive that the clay can be diluted with 500 parts of inert material and the blue colour will still show up when benzidine is added.

Various aspects of the problem are discussed and three principal routes of attack on the heaving shale problem are pointed out—*e.g.*, a minimum water loss, a minimum of base exchange, and a high specific gravity. The former two prevent swelling of the bentonite which causes the heaving, and the latter helps to prevent any movement of the formation into the hole. The use of starch is a new development, and is still in the experimental stage. Those familiar with this treatment have high hopes for its success in the combating of heaving shale as well as the solving of other problems. Also, in very recent months a treatment using sodium alginate has been brought before the industry. A. H. N.

352.* Improvement in Plastering Properties of Muds. H. T. Byck and J. W. Freeland. *Oil Wkly*, 3.2.41, **100** (9), 26.—The paper deals with the colloidal factors affecting plastering properties of muds. The effects of extraneous factors on these properties are also briefly discussed. Experiments are described in which the use of sodium alginate and of Irish moss to improve the plastering properties of muds is studied. Optimum concentrations, method of use, the fermentation of muds containing these materials, and methods of reducing fermentation troubles, effects of high temperatures, etc., are also studied. The conclusions reached consequent on these studies are:

The use of Irish moss or sodium alginate in relatively low concentrations may be expected to improve the plastering properties of muds, to protect them against salt contamination over the range of normal contamination concentration, to permit the use of sea-water to prepare muds of excellent plastering properties, and to permit the use of saturated brine muds, likewise of excellent plastering properties.

Furthermore, special-purpose muds, such as straight-carbonate muds, can be given excellent plastering properties.

For salt concentrations resulting from normal contamination 0·2% protective agent (by weight of total mud) should be adequate; for sea-water muds and saturated brine muds concentrations between 0·2% and 0·6% are recommended.

A field trial of the method has met with success. A. H. N.

353.* Rapid Penetration with High Rotary Table Speeds. Anon. *Oil Wkly*, 10.2.41, **100** (10), 12–14.—Speeds of 450 and 500 revolutions are being obtained with present materials and equipment. While tables are being manufactured and tested at 1000 revolutions per minute, drill-pipe strings permitting continued use of such speeds have not been assembled.

In order to get satisfactory service from equipment at 500 revs./min, it is necessary that many units be synchronized, and several problems remain to be solved before speeds of 750 or 1000 revs./min. can become common.

The kelly assumes a distinctive importance when used with high table speeds, and octagon and hexagon styles are both used. The conventional square kelly is not employed with high table speeds for several reasons, among which is a tendency for mechanical binding at the corners of the bushing that prevents the stem from floating freely through the table while making hole. When unit of a machine is rotating at high speeds, it must possess inherent stability or excessive vibration, and whipping will develop.

The care necessary to apply to the 18-ton drill collars, to the drilling stem and bits, and to the mud system is detailed. When every care is taken, it is possible to drill with high table speeds so that a new connection is required every 12 minutes. Mishaps are not frequent if reasonable precautions are taken. A. H. N.

354.* Principles of Drilling Mud Control. Part 1. S. J. Pirson. *Oil Wkly*, 10.2.41, **100** (10), 21.—The paper forms a co-ordination of available information on the behaviour of drilling muds rather than an original contribution by the author. In Section 1 the origin of clays and general results of weathering processes yielding clays are studied. In the second section the physical properties of clays are reviewed. The primary effect of the weathering process is to reduce the original igneous rocks into small particles, the size of which will vary greatly according to the composition and physical character of the mother rock, the predominant type of weathering, the mode of transportation, and concentration.

A corollary of the extreme division of clay particles is the enormous increase in the extent of the surface of the particles for a given unit weight of clay. The increase in surface is inversely proportional to the diameter of the particles. Thus if a cube of 1 cm. edge length having a total surface of 6 cm. is divided into cubic particles 0·0001 mm. in size, the total surface will be 600,000 cm. But clay particles usually possess a porous or capillary structure, and the increase in specific surface due to the extreme division of clays is even greater than the relation given above. Finely divided particles have the property of forming colloidal suspension with liquids; clays in particular will readily be suspended in water and will form a heterogeneous dispersed system called mud. Due to the great extent of the surface of the particles so dispersed, surface energies and surface forces predominate to the practically complete exclusion of chemical forces. Therefore the chemical composition of the clay particles dispersed in water is of little concern in studying the effect of adding chemicals to a mud. This is extremely fortunate, since many clays of greatly varying chemical composition will react in the same manner to a given chemical. The use of Stokes' Law for measurement of particle size is detailed.

Section 3 deals with chemical properties of clays, and is of interest to mineralogists rather than to drillers. However, the section following deals with the chemical properties of clay suspensions or colloidal suspensions. Materials in this state are distinguished by three properties: (1) a great effective surface or interface; (2) a capacity to fix solids, gases, and ions of salts in solution (strong adsorption); and (3) a tendency to hasten or retard chemical reactions (catalytic effect).

One of the outstanding characteristics of the colloidal complex of clay in suspension is the ability to adsorb cations which are held on the colloidal nuclei in a replaceable condition. The adsorption for cations of the colloidal clay is considerably larger than the adsorption for anions. All cations are not adsorbed to the same extent on the clay particle; monovalent cations are adsorbed according to the following scale of intensity: $Cs>Rb>NH_4>K>Na>Li$, lithium being the least strongly adsorbed of all ions. The bivalent ions are more strongly adsorbed than the monovalent ions according to the following scale of intensity: $Ba>Sr>Ca>Mg$, barium being the most strongly adsorbed. Of all ions, hydrogen is the most strongly adsorbed. When found in nature, clays are not devoid of adsorbed ions. Their presence is undoubtedly responsible for the variable behaviour as drilling muds which is observed in clays seemingly physically alike. Before any two clays can be compared from the point of view of rotary-mud making, it is necessary to know what kind of ions are adsorbed on the clay and in what amount.

The purification of clays from their adsorbed ions by electrodialysis and the characteristics of these ions, together with the concepts of exchange neutrality, exchange acidity, of buffered colloidal electrolytes, and the interpretation of p_H values of clays are all well explained in this long article. A. H. N.

355.* Principles of Drilling Mud Control. Part 2. S. J. Pirson. *Oil Wkly*, 17.2.41, **100** (11), 20.—The fifth section of this paper deals with the physical properties of muds, as these properties are the most important in ordinary rotary drilling. Drilling mud being a heterogeneous fluid, the weight/unit volume is equal to the weight of the liquid + weight of the suspended particles. If the quantity of clay added/gall. of water is known, the density of the mud in lb./gall. (d) is readily calculated by means of the following relation :

$$d = \frac{W_1 + W_2}{1 + \frac{W_2}{8{\cdot}33\rho}}.$$

Weighting materials are discussed, including galena, which has not yet been used for this purpose.

Einstein's equation does not apply satisfactorily to the calculation of mud viscosities, because the clay particles generally do not behave like independent spheres, nor do they retain their original volume ; each of the particles in suspension adsorbs a more or less thick hull of water, which increases considerably the volume of the dispersed phase. However, under certain conditions of treated muds by viscosity-reducers Einstein's equation is observed.

Many factors affect the viscosity of clay suspensions : concentration, temperature, degree of dispersion, solvation, electrical charge, presence of electrolytes, and rate of flow. Each of these factors is separately discussed.

Thixotropy and gelation are defined and their mechanism is conventionally explained. The value of p_H on gelation rate is not settled. Other factors which affect the gelling rate of a clay suspension are : the temperature, the degree of dispersion, the electrical charges, the valence of the electrolytes present, and probably many others as yet undetermined. It has been established that the gel rate will be considerably increased by polyvalent ions. An increase in temperature decreases the gel rate in an irreversible manner. This is important in deep drilling, when a mud may be operating at a fairly high temperature, and should the gel rate and gel strength become unduly reduced there would be danger of the drill cuttings settling during a shut-down period.

The addition of a finely divided clay will increase the gelling rate as well as the gel strength of a drilling mud.

Rheopexy is a phenomenon related to thixotropy in the sense that rheopexy is an acceleration of the gelation rate induced by mechanical action, such as rolling the fluid container around a certain axis or by gently tapping the container. The phenomenon has to do with the orientation of anisometric particles (rod-like or plate-like). The acceleration of the gelling rate may be quite considerable.

Dilatancy, swelling, flocculation, and deflocculation of muds (and methods of stabilizing mud colloids), adsorption of gas or gas cutting, and the filtrability of muds are all studied in some detail, the probable mechanism, methods of enhancing the favourable properties, and means of measuring them being also given.

Six functions of muds of general use and the special problem connected with heaving shales and mudding off producing formations are outlined. Methods of logging muds are briefly reviewed. The exhaustive paper contains a good list of selected references.

A. H. N.

356.* Development of Shooting Practices for Multiple-Zone Completions. R. C. Graham and J. R. Thompson. *Oil Wkly*, 24.2.41, **100** (12), 21–25.—Removable windows are formed of sections of magnesium or aluminium-base-alloy pipe particularly suitable for the application. The magnesium-alloy casing is soluble in acids and to a certain extent in salt water, making its installation of a temporary nature. This type of window is removed by the circulation of inhibited acid, and requires only some means of running tubing, which can be done with a spudder-type drilling machine. However, the aluminium-alloy window does not react satisfactorily to acid treatment for removal. Other methods are described. Finally, the method advanced was the destruction of a magnesium-alloy window by nitroglycerin. This method was suggested not because of the dissatisfaction of the removal by acid, since acid removal had been highly successful, but rather as a means of hastening the completion process. Most sands now producing in the Illinois Basin require a nitro shot to produce efficiently, and if the window could be removed as the sand was shot, a double purpose would be achieved and one step in the completion process eliminated, with resultant savings. Difficulties encountered and methods used to overcome them are detailed.

Three methods of removal by shooting are being used. Apparently each method is accomplishing the desired purpose satisfactorily, with individual operators expressing preference for each method. The first method is to rip the window with a cable-tool ripper prior to shooting. The second is to bridge above and below a window which has not been ripped, and then to shoot it. The third method is to use squibs. This method is gaining popularity rapidly, and will probably supersede methods 1 and 2. A 16-in. squib containing three-quarters of a quart of liquid nitroglycerin is lowered into the hole on the shooter's wire line to a point just above the bottom of the window. A 3-oz. weight is then dropped on the wire line, which detonates the shot. The wire line is then removed and the process repeated 16 in. higher than the first shot. This procedure is repeated until the window is removed. Where a bridging plug has been placed in the lower steel section, the particles resulting from the shot are trapped and removed from the hole with a sand-pump. If this method of shooting does not cause the sand to react as expected, the formation is re-shot similar to method 2, utilizing the bridging plug as a base for the plug-back.

Details and costs are given. A. H. N.

357.* Portability in a Rig Set-up. Anon. *Oil Wkly*, 24.2.41, **100** (12), 39–40.—Methods of reducing down-time while drilling, and of simplifying movement of equipment from location to location, are gaining increased attention from drilling contractors. The set-up described in this paper, used to drill to 5734 ft. in Southwest Texas, employs many features that might be advantageously employed on other rigs.

One of these features is a 92-ft. derrick which breaks down into three sections for convenient movement by truck. A. H. N.

358.* Hydraulic Couplings Promote Flexibility in Power Control of Drilling Equipment. W. A. Sawdon. *Petrol. Engr*, January 1941, **12** (4), 66.—The paper deals specifically with a particular rig using hydraulic couplings and recently used to drill a 10,000-ft. well. From the specific studies certain generalities, however, become apparent.

Of the many points discussed the following deserve special mention. The most experienced drillers frequently stall the engines with a conventional drive, either through improper synchronization of clutch and throttle or in attempting to lift too great a load. With hydraulic couplings installed it is impossible to stall the engines by over-loading. The performance characteristics of these couplings are such that full engine torque is not delivered until they reach a certain speed, which is usually approximately half the rated engine speed. At this point the hydraulic couplings will deliver full engine torque, but will slip as much as 100%. As the engine speed is increased the slip becomes less, until at rated engine speed the slip is between 3 and 4%.

This action permits the hydraulic coupling to be used as a clutch, although in ordinary operation this is not done because of the few seconds' additional time required. In an emergency, however, this feature may be successfully employed. At the other extreme the driller can wait until the hydraulic couplings are at full speed and at minimum slip before engaging the mechanical clutch. If this is done the load may be hoisted with a very rapid acceleration, and lifting time is reduced. Obviously the shock involved by this action is great, and when frequently repeated may ultimately cause some damage to the rest of the machinery.

As slippage is a definite feature of the hydraulic coupling the heat generated during slippage must be dissipated. It had previously been determined that the coupling itself would dissipate the heat accompanying approximately 7–10% slip by convection without the oil becoming dangerously heated. Beyond this amount of slippage the heat generated in the oil induces disintegration, and some provision must be made for cooling the oil. This condition occurs frequently with the mud-pump drives.

The mechanics of the coupling and the scoop-tube for control of speed are well illustrated. A. H. N.

359.* New-Type Boiler Plant for Steam Drilling-Rig. W. A. Sawdon. *Petrol. Engr*, February 1941, **12** (5), 21–24.—The first steam-generating plant utilizing water-tube boilers specially designed for drilling is described and illustrated diagrammatically and photographically. The plant consists essentially of two Foster–Wheeler specially designed water-tube boilers with evaporator, condenser, and three cooling towers. Unit design to provide complete portability is employed throughout, the evaporator and feed-water pump unit and the condenser, feed-water tank, and circulating pump unit for each boiler being mounted on steel skids. Flanged headers are used for connection between units. The portable cooling towers are natural draft units equipped with hose connections to give flexibility in setting up.

The cost of this plant complete is approximately the same as that of the modern conventional boiler-plants now in use for comparable duty. As the boilers use only distilled water and can be operated with any kind of raw water supply, the reduction to a minimum of the expensive troubles caused by bad water is anticipated. Other features considered in selecting the installation include a substantial reduction of fuel-gas consumption, increased safety, lower maintenance costs, and decreased weight and bulk/unit of steam capacity. Under maintenance considerations were the elimination of scale, no stay-bolts to keep tight, and no flues to roll and re-tip. In regard to safety was the fact that there is no appreciable hazard from steam explosion. Conservation of water was also considered ; exhaust steam from pumps and engine is returned to the condenser with an allowance of approximately 10% of the total steam load and leakage and waste to be evaporated from raw water. Should this type of plant be used for barge drilling, no cooling towers would be necessary.

Each item of the equipment used is described separately. A. H. N.

360.* One Derrick Serves Five Wells. J. C. Albright. *Petrol. Engr*, February 1941, **12** (5), 46.—As a part of the programme by which a large number of directional, or " slant-hole " wells are being currently drilled at Huntingdon Beach, California, an interesting plan has been adopted whereby one derrick is made to serve the needs of five wells. Initial investment is, of course, reduced, but a more important reason for devising the multi-purpose derrick was to overcome the handicap of close spacing between the slant-hole wells.

The directional-drilling programme is on a narrow tract on which a number of vertical holes had been drilled in a straight line parallel to the beach several years before. A second row of producing wells, also vertically drilled, is situated near the cliff on the beach side of the boulevard. The need for the slant-hole wells is based on the presence of an oil-zone off-shore, so that the bottoms of wells producing from the formation are about 1500 ft. distant from a vertical line projected through the well-head.

The programme as approved calls for a group of five slant-hole wells to be completed between two of the vertical wells—all to be in a straight line. Ultimately, eighty-five of these wells are to be drilled, consisting of seventeen groups of five wells each.

The derricks, drilling strings, pumping units to be used in production, and metering arrangements are described. A. H. N.

361.* Steel Tanks *v.* Open Pits for Drilling Mud. H. L. Flood. *Petrol. Engr*, February 1941, **12** (5), 106.—It would appear that regardless of the theoretical advantages that steel storage might have, open earthen pits will continue to be used in most drilling operations. Other than in those instances in which steel storage for mud is an absolute necessity, the most valid reason for using steel tanks elsewhere concerns the saving that can be effected in the amount of purchased mud ingredients required.

When a location is to be made in an area where it is known that special attention must be given to mud conditioning, it is suggested that a careful study be made of the cost of steel storage and of the savings that might result from its use. A. H. N.

362.* Welding Tool Joints on Drill Pipe. C. M. Taylor. *World Petrol.*, February 1941, **12** (2), 46–47.—To avoid loosening of tool-joints in service, particularly deep wells, many producers are welding the tool-joints at both ends of every section of pipe. A well-detailed and illustrated account of these operations is given. To appreciate the method of the welding process the diagrams must be studied.

A. H. N.

363.* More Records Established in Wasco Field. Anon. *Petrol. World*, January 1941, **38** (1), 40.—Deep well drilling in record time is described. The total time for drilling three 13,000-ft. wells was 99½ days. Great emphasis is laid on the control of the mud fluid—the largest mud pumps in the world being used. The rig, and equipment, including the four 130-h.p., 350-lbs./sq. in. boilers, are briefly described and illustrated photographically. A. H. N.

364. Rôle of Clay and Other Minerals in Oil-Well Drilling Fluids. A. George Stern. U. S. Bur. Mines. Report of Investigations No. 3556, February, 1941.—This report was prepared with a view to supplying to the clay industry information concerning the types of minerals used in the preparation of drilling mud, their requirements and limitations. It is thus addressed primarily to the non-metallic industry, but at the same time it contains suggestions and ideas which may proved helpful to petroleum production and exploitation personnel.

The data have been collected from a variety of sources, and more particularly during field trips to laboratories where the mud is tested, to producers of the minerals used in making the mud and to actual oil-fields where drilling-mud problems have occurred.

The report embodies *inter alia* sections on the functions of drilling mud, geology and related drilling-mud problems, testing of mud, materials used and control of properties.

In summarizing his findings, the author emphasizes the necessity for carefully controlled mud characteristics, and indicates various methods of measuring clay and mud properties. In particular the filter test is to be recommended as providing a means of measuring how thin a layer of mud will form a film impermeable to filtration of water or other liquid. In other words, it enables an assessment to be made of the ability of the mud to plaster the oil-well sides with a wall-like coating.

One of the chief desiderata of a drilling fluid is that any of its physical properties should be capable of adjustment without appreciably affecting the others. For instance, in certain cases specific gravity can be increased without appreciably affecting viscosity. Optimum characteristics of a drilling fluid can only be determined by careful scrutiny of its functions. Removal of cuttings from the well as rapidly as possible involves a high linear velocity for the mud fluid. To hold the cuttings in suspension and prevent their settling when drilling is temporarily stopped calls for certain gel characteristics which will permit the fluid to thicken when undisturbed. To consolidate loose formations encountered in drilling, the fluid must have adequate density and the quality of building a thin impervious, tough wall in the hole.

Additionally the fluid should be capable of acting as a lubricant and cooling medium for the drill system and bit, it should be easily pumped without too great expense of power, it should not separate on standing and, above all, it should be flexible as regards properties but not susceptible to outside influences such as temperature or the flocculating action of salt-water.

Summarily a drilling fluid should approximate as nearly as possible to the following description. " A low-cost, low viscosity, high density, stable fluid of which no portion will pass through a filter, independent of the flocculating action of salt-water or the influence of temperature variations, and having the unusual characteristic of setting as a gel when allowed to remain quiescent but becoming extremely fluid when agitated."

No one mud can fully comply with these requirements, since certain conditions directly oppose each other. Nevertheless a fluid can be obtained which possesses most of the properties to a fair degree and which is capable of modification to increase any one of the properties.

The amount of clay used in oil-well drilling is great, and some of it is sold at a high price per ton. By far the greatest bulk is, however, of the " back-yard " variety, and is sold at a price only slightly above the cost of handling. Expense is nevertheless involved in technical control of mud characteristics, and it is for the clay industries to recognize that profit lies not so much in the material they have to offer, but in the degree of professional skill and technical expertness with which it is prepared for use in drilling fluids. H. B. M.

365. Patents on Drilling. G. A. Lowrey. U.S.P. 2,229,331, 21.4.41. Appl. 13.2.39. Outside pipe-cutter adapted to cut by rotation and shaped to telescope over a pipe stuck in a well-bore.

L. D. Ekin. U.S.P. 2,229,408, 21.1.41. Appl. 16.2.38. Mechanism for driving pipe for use with the drill-string in the cable system of drilling.

L. R. Croft and C. S. Sanders. U.S.P. 2,229,493, 21.1.41. Appl. 11.1.40. Method and apparatus for completing wells comprising the lowering of a screen during drilling.

C. A. Yeatman. U.S.P. 2,230,280, 4.2.41. Appl. 26.4.39. Hydraulic head integrator of relative vertical motion adapted to be used in drilling-time studies, consisting of a closed liquid container and a pressure recorder.

R. Bassinger. U.S.P. 2,230,447, 4.2.41. Appl. 26.8.39. Well-plug for cementing casing which can be set in a well and removed after the cementing is removed.

A. W. J. Bromley. U.S.P. 2,230,581, 4.2.41. Appl. 30.1.39. Hoisting cable which has a weight-supporting multistrand outer sheet, a non-weight-supporting core, and an electrical conductor inside the core.

D. Breeding. U.S.P. 2,230,522, 4.2.41. Appl. 23.7.38. Well-drilling mast comprising a pair of standards with pulley arrangements at the top.

J. H. Howard and A. C. Catland. U.S.P. 2,230,568, 4.2.41. Appl. 14.10.38. Core-drill for rotary drilling apparatus.

J. H. Howard and W. H. Maxwell. U.S.P. 2,230,569, 4.2.41. Appl. 20.12.39. Roller cutter.

C. H. Miller. U.S.P. 2,230,626, 4.2.41. Appl. 16.8.38. Means for recovering cemented well casings by using a rubber-jacketed casing.

W. Bendeler and C. Howard. U.S.P. 2,230,712, 4.2.41. Appl. 11.4.40. Well-bridging plug.

A. D. Maclachlan. U.S.P. 2,230,723, 4.2.41. Appl. 21.1.38. Hose reinforced by a special reinforcing structure.

D. S. Hubbell. U.S.P. 2,231,123, 11.2.41. Appl. 17.1.39. Cementitious composition characterized by its resilience and strength under dry and wet conditions.

E. L. Knoedler, Jr. U.S.P. 2,231,166, 11.2.41. Appl. 20.6.39. Combustible gas indicator with a wheatstone bridge.

R. W. Schlumpf. U.S.P. 2,231,225, 11.2.41. Appl. 26.2.38. Tool-joint and method of making.

M. E. Norris. U.S.P. 2,231,282, 11.2.41. Appl. 22.1.40. Removable bridging plug for oil-wells.

A. Pfister. U.S.P. 2,231,283, 11.2.41. Appl. 29.7.37. Manufacture of Irish moss.

N. Blihovde. U.S.P. 2,231,284, 11.2.41. Appl. 29.7.37. Purification of Irish moss to obtain a high-viscosity comminuted colloid.

O. F. Simons. U.S.P. 2,231,328, 11.2.41. Appl. 20.11.40. Colloidal suspension of dry extruded fuller's earth having an increase of 50% in its colloidal properties as compared to same earth which has not been extruded.

L. Gitzindanner. U.S.P. 2,231, 421, 11.2.41. Appl. 22.1.38. Colloid mill.

D. G. C. Hare. U.S.P. 2,231,577, 11.2.41. Appl. 29.5.40. Locating cement behind casing by means of mixing with the cement a substance capable of strongly absorbing slow neutrons and using a detector.

K. Burke. U.S.P. 2,231,613, 11.2.41. Appl. 3.4.40. Blow-out preventer and control lead.

A. J. Mason, Jr. U.S.P. 2,231,767, 11.2.41. Appl. 18.12.39. Open-hole support for supporting elements in a desired position in uncased drilled hole.

W. P. Bradley and H. M. Hicks. U.S.P. 2,231,794, 11.2.41. Appl. 23.11.38. Means for protecting pipe-ends.

A. R. Maier. U.S.P. 2,231,840, 11.2.41. Appl. 22.12.38. Travelling block.

J. M. Shimer. U.S.P. 2,231,843, 11.2.41. Appl. 25.9.37. Portable oil-field boiler with a superheater in communication with the smoke box.

A. Boynton. U.S.P. 2,231,878, 18.2.41. Appl. 22.9.38. Threadless drill-stem.

L. O. Koen. U.S.P. 2,231,923, 18.2.41. Appl. 2.12.35. Rotary slip.

W. Pate. U.S.P. 2,232,135, 18.2.41. Appl. 6.2.40. Replacement bearing sleeve for the couplings of drill-stems of oil-wells.

J. C. Fortune. U.S.P. 2,232,172, 18.2.41. Appl. 16.6.38. Rotary drilling snubbing ram.

L. A. Rawson. U.S.P. 2,232,268, 18.2.41. Appl. 12.9.38. Derrick crown construction.

A. R. Barnett. U.S.P. 2,232,360, 18.2.40. Appl. 18.10.37. Apparatus for surveying hose-holes, being a drill-pipe section adapted to receive surveying instruments.

S. E. Diescher. U.S.P. 2,232,593, 18.2.40. Appl. 1.2.39. Welded casing joint.

A. H. N.

Production.

366.* Diesels used in Pennsylvania Repressuring Project. A. C. MacIntyre, *Oil Gas J.*, 6.2.41, **39** (39), 36.—The first diesel-power installation used in secondary-recovery operations was recently placed in use in the middle district of the Pennsylvania fields, where since the early days gas has been generally used. The diesels are being used to permit conservation of natural gas for injection into the sands, where otherwise it would be used as fuel for power.

The plant is described in general terms. A. H. N.

367.* Pumping Equipment. H. F. Simons. *Oil Gas J.*, 13.2.41, **39** (40), 53.—The great bulk of wells in the United States have some type of rod or tubing pump with which to lift the oil. There are approximately 320,000 such wells in the country. Simplicity of operation, ease of adjustment over a wide capacity range, and low operating costs are the principal features of this method.

Plunger-type pumps are generally run on or in a string of tubing, although not necessarily so, casing pumps being quite common in wells where large volumes of fluid must be handled. The recent policy of some companies to drill unusually small-diameter holes has led also to considerable experimentation with the casing pump. Essentially it consists of a beam and rods which actuate a plunger at the bottom of the well. The plunger may be almost as big as the casing, or it may be as small as desired, depending on the amount of fluid to be handled and the size of the rod-string. Where a small plunger is used, the casing pump has no more volume capacity than the regular tubing or rod-pump, the only advantage being the elimination of the tubing string. This advantage is offset by the danger of wearing a hole in the casing due to the repeated contact of the rods as they work up and down. A discussion of surface and subsurface equipment and details of operations to obtain efficiency follow.

Wells which have a high fluid capacity can often be operated economically with a pump which has no rods. There are two main types : bottom-hole centrifugal pumps driven by electric motors, and bottom-hole pumps actuated by hydraulic pressure. These do not need to be run at the bottom of the well, but are so called because they operate while submerged.

The electrical centrifugal pump is run in the well on the tubing with a waterproof cable connecting it to a power supply at the surface. The size of the pump and the size of the motor determine what its capacity will be. For this reason some wells on which high fluid output is expected are equipped with large casing. The hydraulic pump is also run in the well on tubing, but, in addition, it has a macroni string through which fluid (screened oil) pressure, created at the surface by a triplex pump, is transmitted to the pump at the bottom of the well; the exhaust from the pump in the well enters the production string of tubing.

Plunger lift is very briefly described. A. H. N.

368.* Acidizing Gas-Fields. G. Weber. *Oil Gas J.*, 20.2.41, **39** (41), 40.—The history of drilling and developing the Monroe gas-field is given. Recently the greatest well-acidizing programme of the industry was carried out in the field.

A number of the wells treated in the field had open-flow ratings of less than 1,000,000 cu. ft. daily. These were treated in three or more stages, with a usual acid programme of 500 gal. on the first stage and 1000 and 2500 gal. on the second and third stages.

On the larger high-pressure wells in the field, the regular grade of acid was used. In lower-pressure wells, usually below 300 lb./sq. in., shut-in pressure, a low-surface-tension acid was employed. This gave better penetration and, more important, was more readily blown from the formation when the wells were open-flowed. The benefits in using the low-surface-tension acid in such wells was proved by the contrast with a few cases using ordinary treatment. In such cases wells showed little gain in open-flow capacity, and a few showed even lower rates than before treating. Retarded acid was experimentally used, but proved of no particular advantage in chalk rock of the type producing gas at Monroe.

An important result in acidizing in the field was noted in the large amounts of mud which cleaned from some wells after acidizing. Although most such wells had been on production for several years and had been open-flowed at intervals without showing mud, the open-flow following the first acid stage contained quantities of mud together with the spent acid and water. This is believed to be explained by the fact that the acid cuts the mud either in the well-bore or in the formation, where it may be present in the form of a filter cake. A. H. N.

369.* Pumping Practices in Nowata Producing Operations. P. Reed. *Oil Gas J.*, 20.2.41, **39** (41), 42.—Operations in water-flooded fields are characterized by the individuality of each operation, in that even in the same property different methods are used. Thus while one operator decides to change from well pumping with time-controlled electric motors to central pumping, another reverses the procedure and changes from central pumping to the single-well pumping practice. In another field one row of centrally pumped wells alternates with another row of wells which are individually pumped.

For the requirements of numerous producers in the field, gas engines prove to be well adapted for economical operation. On the other hand, electric power has certain features which have been found to be desirable for water flooding. In fact it may be said that three of the conspicuous aspects of water-flooding operations in the last 5 years at Nowata have been the increased use of electric power, successful exploitation of reserves of siliceous lime-water by several operators in the area, and the economic advantages offered by the practice of producing water-flood production by flowing.

A. H. N.

370.* Recent Trends and Success of Plugback Work in East Texas. W. H. Wiginton. *Oil Gas J.*, 27.2.41, **39** (42), 64. *Paper Presented before American Petroleum Institute.*—The paper discusses briefly the older methods and gives a more complete discussion of the newer methods used in plugback work to shut off salt-water, showing past results of various methods that have been employed, and outlining the economics of this type of remedial work.

The cost of a majority of the workovers in the past has been entirely too high to justify the work—therefore the various operators have demanded that less expensive methods be developed whereby salt-water production can be profitably curtailed.

The older methods in use are: (1) pump bailer; (2) displacement; (3) bradenhead squeeze; (4) short-string squeeze; (5) retainer squeeze.

The more recent methods in use are: (1) removable cementing tools; (2) formation packers; (3) bridge plug or hook-wall packer between perforated zones. A new removable cementing tool offered by several service companies consists of cups and slips with a by-pass joint on top of the tool. On application of hydraulic pressure the cups expand thereby keeping the pressure off the casing. The slips are necessary to hold the tool and tubing or drill-pipe in the hole while the pressure is on the formation. After the required amount of cement is placed in the formation the tool is released, the excess cement is washed out by reverse circulation, and pulled out of the well. No appreciable amount of cement returns after the tool is released if the final pressure obtained is from 1800 to 3000 lb./sq. in. on the pump. Details are given.

A formation packer has been developed to provide an adjustable and removable pack-off between an upper and lower producing formation, where it may be impossible to predetermine exactly the most effective pack-off point. Some of the factors affecting the most desirable location of the packer which may be difficult and expensive to determine are: the absence or presence of a definite shale-break and its definite location; the size of hole below the casing seat; the condition of the well-bore in regard to caves, washes, etc., and by means of the formation packer, the pack-off point can be adjusted to give the most effective shut-off.

The third method is used where the oil-string is set through the sand section and the original completion of the well is through perforations. After water starts to enter the well, a higher zone is perforated and some type of bridging plug or hook-wall packer set between the two perforated zones.

Economics of remedial work is studied in brief, but the methods are well illustrated and detailed. A. H. N.

371.* Seven-Year Trial Proves Gas-Injection Project Profitable. Anon. *Oil Wkly*, 3.2.41, **100** (9), 16–20.—Injection of gas is being used primarily to increase the ultimate recovery, the immediate objective being control of reservoir conditions through input volumes and pressures. Both water encroachment and depletion towards an uneconomic operating level are being retarded by repressuring in a manner similar to recycling. By the time the last well is plugged the field will have produced 3000 brl./acre in excess of the recovery anticipated without repressure control. The history of the field—Cotton County, Oklahoma—is given.

The decision to repressure resulted from two individual factors. In the first place, water became a threat as early as 1932. While most of the water was coming in from the edges, due to decreased formation pressures, there was some water in the pay formation at different levels, to indicate that a complete separation of water and oil had been doubtfully established in the reservoir. This water could not be made subject to control, but the migration from the edges of the dome could be held back, or at least allowed to encroach only as the oil was produced, by suitable pressure control. The second factor was the apparent certainty that with normal production, and subsequent additional lowering of the already low formation pressure, reservoir pressure differentials would result in swift encroachment of edge-water that would trap large volumes of oil in the loose sand-body.

As most of the wells had been drilled on a 10-acre plan, the block could not be developed with gas injection as a prime influence. In view of the desired control over formation-water, no strict adherence to a uniform spacing for injection wells was made. Instead, the injection wells, some old producers and some new wells for that purpose, were selected on the basis of their adequacy. This was judged on the degree of encroachment in a particular area, the oil present, reservoir energy locally available, water–oil ratio, and the thickness of the pay at the spot. On such basis a plat would indicate somehat haphazard spotting of the injection wells, and not the more practical operating balance obtained by adjusting their location to meet reservoir conditions. The compressor plant, distribution system, and gas manifolds are described.

A.P.I. gravity of the oil showed an increase, as well as the production recovery.
A. H. N.

372.* Sampling Distillate Wells. K. E. Cody and D. M. Luntz. *Oil Wkly*, 17.2.41, **100** (11), 17–18.—One of the satisfactory methods of obtaining an accurate analysis of the raw well-gas is to flow the stream into a high-pressure separator, collecting and analysing samples of the separator vapour and liquid. A diagram and typical calculations illustrate the method. By compositing these two analyses according to a material balance on the separator, the analysis of the raw gas is obtained. This method of procedure naturally requires the metering of both the dry gas and the liquid.

It is possible in most instances to take a representative sample of the raw gas directly from the well-head before the choke. However, such a sample is very difficult to handle in the laboratory, and this method will not give enough distillate for a complete evaluation unless the sample is continually drawn into a small separator and the gas and liquid are measured and handled as described above. The latter method is generally used in connection with portable testing units.

Samples of raw well-gas should never be taken from the line between the choke and the separator, as the throttling effect of the choke changes the gas from a substantially homogeneous mixture into a liquid–vapour mixture. Sampling such a system is extremely difficult, if not impossible.

To illustrate the information which should be available in a complete distillate evaluation, a specific work-sheet is presented, with explanations of the various operations and results.
A. H. N.

373.* Re-working Wells. E. S. Post. *Oil Wkly*, 17.2.41, **100** (11), 34.—Re-working in South Texas fields has been found to pay dividends. An almost set practice is followed. A portable spudder type of rig is moved over the location and rods, tubing, and remainder of the pumping unit are removed from the hole. The liner also is fished out and the well bailed down dry as possible. A sand-pump type of bailing unit is used to remove all sand, shale, sediment, etc., from the hole. If there is an excessive amount of gas, the hole is filled with clean oil and the sand-pump is worked at the bottom of the fluid load. No water is put in the hole at any time, as the shale and bentonite content in the formation expands rapidly, thus requiring a greater amount of bailing to finally clear the formation.
A. H. N.

374.* Acid-Soluble Cement as an Aid in Increasing Flow Through Gum-Perforations. W. A. Sawdon. *Petrol. Engr*, January 1941, **12** (4), 33–35.—The acid-soluble cement is made by mixing approximately equal parts of any type of oil-well or Portland cement with a specially prepared calcium carbonate. The latter chemical differs considerably from that now being used for conditioning mud-fluid prior to acid treatment for removal of the mud-sheath from the wall of a producing sand.

Although evidence is still lacking on which to base definite requirements concerning the strength of cement for different oil-well jobs, a reduction in shrinkage is always desirable, as excess shrinkage may not only cause cracking, but will tend to weaken the bond between the cement encasement and the wall of the hole. The shattering of the cement around the pipe by the action of the tools going in and out of the hole is believed by some engineers to be a frequent occurrence, particularly when the clearance is small; it is asserted that tests have indicated the acid-soluble cement to show less shatter than neat cement.

Another factor that may have an influence on the success of a cement job is the scouring effect on the walls of the hole that probably accompanies the abrasive action caused by the calcium carbonate in the slurry.

The quantity of set cement that can be dissolved with any unit volume of acid is fixed, and depends on the area of contact of the acid and the cement. The amount of cement dissolved is therefore less when the area of contact is small than when the area of contact is large, and as the acid spends itself a protective coating is formed on the cement that inhibits further action. When acidizing via a hole through this cement there is thus no danger of the action of the acid extending to a point where the effectiveness of the cement as a water shut-off will be impaired.

Procedures of utilizing this cement, as well as test data on its properties, are given and illustrated graphically. A. H. N.

375.* Practical Application of Planned Optimum Rate Proration. Pt. 2. A. M. Crowell. *Petrol Engr*, January 1941, **12** (4), 54.—Following the discovery of a new pool, reservoir pressure tests are conducted on representative wells by the engineers as development proceeds. These key wells are selected for their structural position, and must be so spaced that the areally weighted reservoir pressure obtained will be representative for the pool as a whole. Once selected, these same wells remain as key wells during the life of the pool. After a shut-in period of not less than 24 hr., each well of the key-well group is tested at regular intervals with standard subsurface pressure gauges.

The bottom-hole pressures obtained are then posted on a map at the points representing the well locations; the map is contoured in 50-lb. intervals and planimetered so that the areally weighted reservoir pressure may be arrived at. The individual pressures of the wells not tested are read from the map by interpolation.

Briefly, changes in reservoir pressure and in gas–oil ratio determine the production quota fixed for any pool for a given period. If, in a water-drive pool, a decline in reservoir pressure is registered for two consecutive periods, the quota for that pool is restricted until the pressure decline is arrested.

In the case of a gas-drive pool where pressure decline is a normal function of withdrawal of oil and gas, an abnormal acceleration of decline may result in the commission further restricting gas–oil ratio allowances.

Very soon in each oil pool the most efficient rate of production can be determined within 10% or 15% of the optimum. As soon as this rate is determined, a top allowable is set, subject only to minor adjustment as additional units are brought into production.

Under this system of fixing optimum rates of production, market demand plays only a secondary rôle. Inasmuch as the inefficient or unnecessary storing of oil is prohibited, it is impossible to exceed the bona-fide market requirements for oil from the fields under control without violating the law.

The paper is detailed in treatment and is concluded with an appendix regarding the Oil and Gas Conservation Law for Arkansas. A. H. N.

376.* Use of Electric Power Increases in all Phases of Petroleum Industry. H. E. Dralle. *Petrol. Engr*, January 1941, **12** (4), 72.—Electric drive has proved particularly suitable for providing increased power for drilling because of its flexibility. For maximum performance there is a noticeable trend towards the direct-current variable-voltage system of control. It is mobile, self-contained, and flexible, and on many large rigs the generators are designed to prevent stalling the engine under any operating conditions. By adding suitable units for parallel operation as well as capacity to the draw-works motor, it is practicable to obtain any amount of power for hoisting within the mechanical capacity of the rig. The best practice seems to dictate the use of 1 kw. of generator capacity for each h.p. of motors connected, for any operation.

In oil production using electrified drives there is a definite trend to automatic pumping by time-switch control. This is used not only on wells of small volume requiring occasional operation, but also on wells that are pumped intermittently in compliance with proration schedules.

Time switches can be preset to start and stop wells on any cycle from once each 24 hr. to once each quarter of an hour. Many pumping units now employ a weather-proof motor and control of the type that utilizes time-switch operation, and high-torque motors ensure oil-well starting even under adverse weather and well conditions.

When central station power is not available a popular method of obtaining electric power is from a self-contained, engine-driven, power unit.

The paper further deals briefly with the use of electric power in refineries, recycling plants and pipe-lines cathodic protection. A. H. N.

377.* Electric Power Provides for Flexible Expansion as Well-Pumping Needs Increase. H. L. Flood. *Petrol. Engr,* January 1941, **12** (4), 27–28.—The factor of flexibility requirement is recognized as being especially important in the East Texas field because of the erratic performance of wells, even when side by side and producing from virtually the same depths in the woodbine sand. On the same lease being discussed, two wells now pumping may be separated by another well still flowing—all producing from the same depth. It was this factor of flexibility that largely dictated to the companies operating in East Texas the use of electric central plants. Although motors have been installed having capacity to serve the increasing power requirements of the wells for some time to come, and consequently are in all instances larger than the wells in their present condition require, full benefit is derived from the ability to combine all the smaller individual current consumptions of the several wells. This permits satisfactory operation with much less installed horse-power in the generating plant than would be possible if, say, individual engines were installed at each well having the same provision for future needs of the wells.

The generators, distribution system, and individual well equipment are briefly described. One of the advantages of electric power for pumping that is welcomed by the production engineer responsible for maintaining efficiency of the producing units is the facility with which the well can be accurately studied and its operation judged. The simplest manner by which this may be done is to use an indicating ammeter to observe the amount of current consumed at various phases of the pumping cycle. If recording instruments can be made available, a " card " should be obtained that will divulge information concerning the well as accurately as other forms of dynamometers.

A. H. N.

378.* Conservation and Economics of Gas-Condensate Fields. J. O. Lewis. *Petrol. Engr,* February 1941, **12** (5), 51.—The method of operating a gas-condensate property is to produce the gas, pipe it to an extraction plant, extract the fluids, recompress the gas, and inject it underground, preferably into the same sand. The extraction plant may be simply a system of gas separators and coolers with a stabilizing unit that will extract some 80% of the liquids, or it may be an expensive refrigeration or absorption plant that will recover more than 95% of the liquids, even the butanes. The investment consists of the cost of discovering the field and acquiring the land, the cost of wells, the cost of the extraction plant and the cost of the compressor plant. The parts are inseparable, and the output must pay a return not only on the property and the wells, as does an oil property, but also on the plant and the expenses of operating it. The wells are costly, for gas-condensate fields are found in deep sands.

Because the condensates exist underground as vapours, often in concentration of less than 1 gall./M cu. ft. of gas, the condensates contained in an acre of sand are much smaller in volume than the oil in an oil-sand of equal thickness, area, and porosity. If it were necessary to drill wells to the spacings customary in oil-fields, it would not be profitable to develop a condensate field, and it would remain a frozen asset; but gas moves much more readily through a sand than does oil, consequently the wells can be spaced much farther apart. The percentage of condensate recoverable in a moderately uniform sand will be little influenced by the number of wells, but rather by their structural positions and geometric pattern. Spacings of as much as 300 acres/well have been used, and even wider spacings could have been used, were it not necessary to provide a sufficient number of outlets so that the gas may be extracted at legal rates within a reasonable period of time.

Operations in Texas and economics of cycling are discussed. A. H. N.

379.* Problems in Condensate-Type Production. R. L. Huntington and C. Schmidt. *Petrol. Engr,* February 1941, **12** (5), 68.—Production practice and principles of keeping the fluids in a single vapour phase in condensate fields are briefly reviewed.

The drilling of wells on 10-acre tracts would be entirely out of the question in most distillate fields. In the first place, the total value of recoverable condensate would probably not equal the first cost of such intensive development. Furthermore, the effective drainage of widespread acreage will take place in single-phase fluid or condensate fields in much the same manner as in gas-fields. Although two wells (one for cycling and pressure maintenance, and the other for withdrawal of condensate-bearing fluid) might eventually produce substantially all the condensate from a lease several square miles in area, it is unlikely that the time rate of pay-out would be fast enough to attract investors into such a proposition. It is more probable that the spacings will be of the order of 80–320 acres, depending on the allowables and the fluid content of the particular reservoir in question.

Recovery processes are very briefly described. Data from experiments on the mixing of gases in such fields show that the mixing rate is an inverse function of pressure.

A. H. N.

380.* Testing Condensate-Type Wells. G. O. Kimmell. *Petrol. Engr*, February 1941, **12** (5), 76.—As tapped, most condensate-type reservoirs are in a state of " saturation " or at their " dew-point." Three distinct types are known : (*a*) reservoirs at their dew-point isolated from any associated oil, (*b*) " under-saturated " reservoirs isolated from any associated oil, and (*c*) saturated or dew-point reservoirs (or gas-caps) overlying an oil-saturated zone.

There is a fourth type of reservoir producing through " dry gas wells " that would exhibit retrograde phenomena were the gas subject to proper temperatures and pressures never encountered in normal production. Graphs show the effects of pressure and temperatures on each type.

Condensate well characteristics are discussed. The pressure rise in a condensate well reaches a maximum, after which it declines. Two factors control the shape of pressure build-up curves : (1) ability of the reservoir pressure to " neutralize " the resistance between the reservoir and well-head, and (2) the physical changes along the resistance after shut-in. The pressure-rise part of the curve is controlled by (1), and the pressure-decline part by (2). The controlling physical change is that of increased density of the vapours in the conductor as it cools off. Pressure build-up curves will tend to coincide after a time, provided the reservoir pressure is not reduced during the period over which the data are compared.

Methods of sampling are described in some detail, and these are followed by procedure for analysing the samples.

Preliminary tests have proved that it is possible to develop small-scale equipment for all the following types of investigations : (1) direct measurement of reservoir conditions that would provide data for the development of the useful parts of the " pressure–temperature-phase " diagram. (2) Examination at extremely high pressures of the effects of counter and concurrent absorption on extraction efficiency, and examination of various absorption mediums. (3) Low-temperature, high-pressure studies. (4) Thermodynamic properties such as specific heats, Joule–Thomson effects, and film coefficients. A. H. N.

381.* Well-Completion Methods in Condensate Fields. Anon. *Petrol. Engr*, February 1941, **12** (5), 94.—One of the most important considerations in completing either a producing or injection well is to provide a clean, unobstructed formation face opposite the section of casing that is opened or perforated. Uncased hole is not considered advisable in wells that are to be used for the injection of gas, on account of possible caving and sloughing-off.

The cleaning of injection wells may be accomplished in three ways. The method to be used depends largely on the conditions existing. The first and simplest method is to back-flow a well at a rather rapid rate for a short interval. The high velocity of gas leaving the face of the formation imparts a beneficial cleaning action.

The second method is to wash the well with clear water, then unload and back-flow. This method will often remove mud filter-cake that otherwise plasters the sand-face.

The third and most effective method is to give the wells a treatment of mud acid. The acid is pumped into the well, allowed to stand the proper time, and the well then back-flowed. This type of treatment has been used in deep high-pressure operations with much success. Wells treated have nearly doubled their intake capacities and the working pressures required have been greatly reduced.

To reduce capital investment, dual and triple completions are fast becoming standard practice in multiple-zoned pools. Dual and triple completions are in general use in California and Illinois. Dual completions are used in Texas and Louisiana and on a few installations in Kansas. Details of these are given. A. H. N.

382.* Physical Properties of Hydrocarbon Mixtures in Condensate Production. F. H. Dotterweich. *Petrol. Engr*, February 1941, **12** (5), 98.—A study on binary mixtures with components of complete mutual solubility, in all proportions, produces complicated results when investigated. In addition to variations in temperature, volume, and pressure, a fourth variable is encountered—that of composition. Phase relationships are explained with the aid of diagrams giving the effects of variations in three of these four variables on the fourth.

To illustrate retrograde condensation examples are given, one of which is the following : when a mixture is tested at 35° C., the liquid phase appears at a pressure of 43 atm. (630 lb./sq. in.). As the pressure increases the liquid will increase to a certain point, after which this procedure is reversed and the liquid phase decreases until at a pressure of 93·5 atm. (1375 lb./sq. in.) it completely disappears and only the gaseous phase appears. This experiment at 35° C. and varying pressures on such a hydrocarbon mixture illustrates the phenomena of retrograde vaporization of the first type. Should the experiment be repeated at 35° C. but beginning with a pressure greater than 93·5 atm., only the vapour phase would be present. Should the pressure be dropped to 93·5 atm., the liquid phase would appear and increase with lower pressure in the retrograde range, and this procedure may be referred to as retrograde condensation of the first type. Other types of retrograde systems are similarly detailed.

Graphs of equilibrium vaporization constants for gas mixtures are given and their significance is detailed.

Single- and multiple-stage separation are discussed. An interesting point noticed is that at higher pressures it is found that the volume of liquid becomes more nearly the same for different temperatures of separation. In addition, with single-stage separation at pressures higher than 2500 lb./sq. in., it is possible to obtain greater recoveries at higher temperatures or, in other words, there is a retrograde temperature effect.

A. H. N.

383. Patents on Production. T. W. Murray. U.S.P. 2,229,115, 21.1.41. Appl. 24.6.39. Pumping and drilling unit comprising a motor, a driven shaft, variable-speed and reduction gearing, a crank-arm at each end of the shaft and flexible means driven by the crank arms for operating the pumping rods.

H. T. Kennedy and A. J. Teplitz. U.S.P. 2,229,177, 21.1.41. Appl. 26.5.39. Water shut-off in oil- and gas-wells by means of plugging material the action of which is inhibited in the pay-zone but allowed to proceed in an adjoining water-sand.

H. H. Greene. U.S.P. 2,229,325, 21.1.41. Appl. 3.8.40. Deep-well bridge.

J. A. Pate and C. L. Pate. U.S.P. 2,229,519, 21.1.41. Appl. 2.8.37. Releasing pump-plunger.

J. A. Zublin. U.S.P. 2,229,538, 21.1.41. Appl. 1.5.39. Method of producing oil and gas from a well consisting of agitating and releasing gas from the oil, driving back the gas to an oil formation and producing the oil.

J. A. Zublin. U.S.P. 2,229,539, 21.1.41. Appl. 1.5.39. Method of and apparatus for producing oil and gas from a well whereby the gas and oil mixture is compressed before the gas is released for reinjection in the formation.

J. A. Zublin. U.S.P. 2,229,540, 21.1.41. Appl. 1.5.39. Method of repressuring oil- and gas-wells.

J. A. Zublin. U.S.P. 2,229,541, 21.1.41. Appl. 12.5.39. Apparatus for pumping oil-wells containing agitating means to separate the gas from the oil and pump the separated oil to the surface.

H. L. McLaughlin. U.S.P. 2,229,581, 21.1.41. Appl. 15.10.37. Well-shooting bridge.

M. T. Works. U.S.P. 2,230,421, 4.2.41. Appl. 7.6.38. Pipe hanger for a well-head.

D. L. Katz. U.S.P. 2,230,619, 4.2.41. Appl. 18.3.35. Process for separating gas and oil issuing from an oil-well so that the gas will be dry and the oil will contain all the gasoline constituents originally present in the crude.

G. Swain. U.S.P. 2,230,787, 4.2.41. Appl. 4.6.35. Fluid-actuated pump.

C. J. Coberly. U.S.P. 2,230,830, 4.2.41. Appl. 5.3.35. Deep-well pump and method of installing and removing the same.

V. L. Andrew. U.S.P. 2,230,856, 4.2.41. Appl. 10.12.38. Pitless pump adapted to be fixed in a well-casing.

H. M. Loeber. U.S.P. 2,231,131, 11.2.41. Appl. 14.6.37. Deep-well pump.

L. L. Rector. U.S.P. 2,231,221, 11.2.41. Appl. 1.6.37. Packing device.

J. P. Sullivan. U.S.P. 2,231,303, 11.2.41. Appl. 30.3.39. Pump.

A. W. Steenbergh. U.S.P. 2,231,417, 11.2.41. Appl. 11.2.41. Intermittent gas-lift control with a spring-controlled valve and an impact means actuated by the flow of the liquid to open the valve.

M. L. Johnston. U.S.P. 2,231,425, 11.2.41. Appl. 14.7.39. Oil-well testing device for testing formations.

M. De Groote. U.S.P. 2,231,752 and 2,231,753, 11.2.41. Appl. 20.2.39 (both). Processes for resolving petroleum emulsions by means of water-insoluble salts of basic alkylamines.

M. De Groote. U.S.P. 2,231,754, 2,231,755, and 2,231,756, 11.2.41. Appl. 13.7.39 (all three). Processes for resolving petroleum emulsions of the water-in-oil types.

M. De Groote. U.S.P. 2,231,757, 11.2.41. Appl. 23.10.39. Process for resolving petroleum emulsions of the water-in-oil type.

M. De Groote. U.S.P. 2,231,758 and 2,231,759, 11.2.41. Appl. 26.1.40 (both) Processes for resolving petroleum emulsions of the water-in-oil type.

R. T. Smoot. U.S.P. 2,231,820, 11.2.41. Appl. 30.3.40. Pump.

E. T. Adams. U.S.P. 2,231,861, 18.2.41. Appl. 27.9.38. Well-pump.

W. L. Bald. U.S.P. 2,232,199, 18.2.41. Appl. 25.1.40. Hydraulic oil-well packer.

J. M. Hamilton. U.S.P. 2,232,325, 18.2.41. Appl. 18.5.40. Well-packer.

O. F. Ritzmann. U.S.P. 2,232,476, 18.2.41. Appl. 27.11.39. Method and apparatus for measuring depths in wells by means of high-frequency explosive sounds.

See also Abstract No. 341. A. H. N.

Transport and Storage.

384.* Cathodic Protection of Oil Storage Tank Bottoms. D. H. Bond. *Petrol. Engr*, March 1940, **11** (6), 100–102.—Normally cathodic protection is thought of as applying to pipe-lines, and when extending the method to cover tank bottoms the relatively large area to be protected must be borne in mind. An 80,000-barrel tank with 10,700 square feet of base is equivalent to 6171 ft. of 6-in. pipe.

Once the D.C. amperage for complete protection has been decided on, the type of equipment to be used must be chosen so as to take into account the various contradictory effects. For ground beds of given resistance the larger the number of units installed the less will be the power required to give the total amps. Further, better current distribution will be provided, thereby reducing the amount of ground-bed cable required. Against this there is the increase in cost of installation as more units are used and higher maintenance costs. Similarly the choice of generators or rectifiers for the production of the D.C. current will depend on the type of power and labour available.

In a given case, satisfactory protection was afforded to a Gulf Coast tank-farm containing forty-five 55,000-barrel tanks, that had suffered serious corrosion in the past, by the installation of 4 units with a rating of 15 v. and 100 amps. each. These units were motor generators driven by 220-v. 3-phase electrical power available at the farm. The ground-bed resistances varied from 0·122 to 0·208 ohms, and consisted of lengths of 8-in. pipe buried horizontally, together with lengths of 6-in. pipe buried vertically.

From the estimated cost of this installation it was apparent that a considerable annual saving would be made—in fact, the elimination of reconditioning each tank at 10-year intervals would pay for the installation in one year.

Assuming that the potential of the protected surface must be at least 0·80 v. negative to ground, all the tanks except one were fully protected, as were all connecting pipes and coated incoming and outgoing trunk-lines for 1½ miles from the property.

T. T. D.

385.* Protective Coating on Above-ground Pipe-Line Structures. C. F. Rassweiler. *Petrol. Engr*, March 1940, 183–186.—In the painting of storage tanks, protection from corrosion at minimum cost is no longer the primary consideration. The controlling factor is now the necessity of reducing evaporation losses by using paints of high reflectivity. In choosing these, average light reflection is of more importance than the initial value, but, especially in the case of tank whites designed to disintegrate by gradual surface erosion, the factors of annual maintenance cost and length of protective life are still important considerations. Proper preparation of the surface by adequate metal cleaning, and selection of a primer, which not only has a good inhibitive effect but also has good durability when exposed by the eroding top-coat, will ensure that repainting will only become necessary when the top-coat has chalked thin enough to affect appreciably light reflectivity or appearance.

If the paint is to withstand such exposure to water and chemicals that the use of special materials is justified, recourse may be had to : (1) bituminous finishes, (2) the alkyds, (3) the phenol formaldehydes, (4) the chlorinated rubbers. Type (1) have outstanding resistance to water and chemicals, but poor durability to normal weathering. They are most effective when applied in thick, hot coatings, but these have a poor appearance. Type (2) have the best properties when normal weathering is the important factor and exposure to water is intermittent and strong chemicals are absent. Type (3) have outstanding resistance to water or mild chemicals, especially mild acids, but not to strong alkali. Their most effective use is totally submerged or where normal weathering is less important than other effects. Type (4) are inert to water or relatively strong acids or alkalis. In a moist atmosphere, however, their use is of questionable value above 150° F. They are the most expensive per unit of film thickness and, owing to their high viscosity, difficult to apply. They are most useful under conditions too severe chemically for the phenolic finishes.

Especially on areas exposed to water and chemicals, great attention must be paid to cleaning the surface of the metal. Unless rust and chemicals are thoroughly removed, it must be realized that painting will merely improve the appearance and have relatively little value in preventing corrosion. Particular attention must also be paid to application on these areas, which are liable to be badly roughened, and care must be taken to see that an adequate thickness of paint is piled up over the rough sections. It is also vitally important that the surfaces involved should be kept clean and free from water and chemical spray during the period of cleaning and priming, the application of subsequent coats, and until the finish has had adequate time to harden.

In the painting of galvanized-iron surfaces, modern practice is not to allow preliminary weathering ; when repainting is done, the same cleaning precautions should be followed as are ordinarily specified for steel. The painting is obviously useless unless materials are used that will adhere permanently to the zinc surface. Primers of this type are now available, containing zinc dust incorporated in a special vehicle. It has been shown that water-soluble soaps tend to form at the zinc-paint interface and, aided by moisture coming through the paint film, destroy adhesions of the paint coatings. The zinc dust in the primer presumably causes these zinc soaps to form in the primer itself rather than at the interface, so that adhesion is not affected.

T. T. D.

386. Modern Practices in the Protection of Pipe-Lines against Corrosion. S. Thayer. *Petrol. Engr*, Midyear 1940, **11** (10), 131–133.—The author describes various methods which are now in use to minimize pipe-line corrosion.

Construction of New Lines.—(1) A careful soil survey is made to determine the coating procedure. The pipe-line is then entirely coated except where it passes through soil known to be definitely non-corrosive. The success of this method depends on the care and experience of the soil examiners.

(2) New lines are entirely coated. This is probably a somewhat wasteful method, but eliminates the difficulty of knowing with certainty which soils will give trouble.

(3) Lines are laid unprotected and "hot-spots" which develop later are replaced by new coated line. This may prove expensive, especially if the "hot-spots" are numerous or extensive in area, but in many cases will be less than the cost of coating the entire line.

(4) Lines are laid bare and either the "hot-spots" protected electrically as they develop, or the entire line is so protected. In the author's opinion it is bad practice to lay a bare line and then install electrical protection, as the cost would be considerably more than the cost of coating plus the cost of equipment to protect a well-coated line.

(5) In a few cases the lines are well coated and electrical protection installed immediately. Any faults in coating that may occur will then be protected. If the coat is highly resistant and the faults not too large in area, a very small current is required for protection, one small unit being sufficient to protect at least 5 miles. This method should prove extremely efficient.

Maintenance of Old Lines.—(1) Affected line, as determined by frequency of leaks, is replaced by new or reconditioned pipe, generally coated. Care must be taken that the replacement extends well beyond the affected area. This method is liable to be expensive.

(2) Electrical protection is installed as necessary to cover affected areas. This has proved an excellent method, although obviously not practicable for very small pipe-lines where the affected areas are only a few feet in length.

(3) Instead of waiting for the occurrence of leaks, surveys are made to determine where the pipe is most affected. Several methods for making these surveys are in use, all depending to a greater or lesser extent on the skill of the examiner. They include tracing the electrical currents on the pipe to the points of discharge into the soil, analysis of the soil to determine suspected areas, and examination of the pipe where, in the opinion of the examiner, the poorest pipe is likely to be found. From the results of these surveys, the steps necessary for suitable protection must then be decided.

(4) Electrical protection is installed, where convenient and inexpensive, regardless of the state of the pipe. Units are installed at booster stations and the protection forced to extend as far as possible in both directions. This method has proved to be almost ideal in a particular case, but is probably not so easily adaptable to other systems.

The remainder of the article was devoted to a comparison of the merits of various types of units used for electrical protection including rectifiers, motor generators, windmills and engines.

T. T. D.

Crude Petroleum.

387. Analyses of some Illinois Crude Oils. H. M. Smith. U.S. Bur. Mines. Report of Investigations No. 3532, December 1940.—By virtue of important discoveries of new oil-fields made in 1937, Illinois is now one of the most prolific oil-producing areas in the United States. This report embodies the results of analyses of thirty-five samples of petroleum from these new fields, and also includes analyses of seven samples from fields developed before 1936. The samples analysed represent three geographically different producing areas in the State—namely, the eastern boundary in Clark, Crawford, Lawrence, Edwards, Wabash, White, and Gallatin Counties; an area

25 miles farther west in Clay, Richland, and Wayne Counties and the north-western corner of White County; and the south-central area in Fayette, Marion, Clinton, Washington, and Jefferson Counties.

Of the forty-two samples analysed only four show marked deviations from the general average, the others being similar to Oklahoma City crude oil, except that they are slightly more naphthenic and have a somewhat higher sulphur content.

Included in the report is a table listing the samples in order of increasing sulphur content, and from this it becomes apparent that most of the high-sulphur oils are found in the group of fields along the eastern border of the State and, further, that no low-sulphur oils are found in that area. In fact, if a division is made between those having less than 0·18% sulphur and those having 0·18% or more sulphur, none of the samples from the eastern area will fall into the first group. Similarly all the samples from the area farther west in Wayne, Richland and Clay Counties will fall in the second group, and only six of the remaining samples from the south-central area will fall in the second group.

The question is raised as to whether a more extended survey of Illinois crude oils would corroborate this apparent segregation of high-sulphur oils. H. B. M.

388.* Talco-Treating Methods Provide Fuel Economy and More Settling Time. G. Weber. *Oil Gas J.*, 10.3.40, **39** (21), 34.—A description is given of various methods of water removal from the heavy asphaltic Talco crude. The particular problem in this field is the lack of gas, necessitating the purchase of fuel gas for the treating of the crude. In general, the maximum amount of water is separated by settling, and chemical treatment using 1 qt. to 25 qts. for 1000 brl. oil is then carried out at 120–130° F. Hay-tanks consisting of baffles, excelsior section, and heaters are still used in the field, in addition to more modern methods. Heat conservation is effected by preheating in stack and return stream exchanges, utilization of non-condensible vent-gases from flumes and lease tanks, and utilization of heat in exhaust gases of pumping engines. C. L. G.

Cracking.

389.* Improved Processes in Manufacture of Motor Fuels from Petroleum. G. Egloff. *Petrol. Engr*, Midyear 1940, **11** (10), 21–26.—The primary function of cracking is to increase the quantity and improve the quality of the gasoline that can be obtained from a crude. The success of this process may be gauged from the fact that, on cracking, an average yield of 45% is obtained from crude, compared with 21% straight-run. Further, an average octane number for cracked gasoline is 70, whereas straight-runs are sometimes as low as 15.

In the case of thermal cracking, at temperatures of 900–1100° F. and 1000 lb./sq. in. pressure, octane numbers average about 70 from charge stocks of gasoline, naphthas, or heavy oils. To produce gasolines of higher octane number, catalytic cracking is available. Catalytic reforming of gasoline or naphthas at 950° F., and low pressure, may yield upwards of 80% of 80-octane-number gasoline. The gases obtained as by-products are much richer in olefines than those obtained from thermal cracking. These gases are converted into high-octane fuels either at high temperatures and pressures, or catalytically in the presence of phosphoric acid at low temperature and pressure. In this way the butane–butene fraction is catalytically polymerized to yield *iso*-octenes, which are hydrogenated to *iso*-octanes.

iso-Octane is also manufactured by catalytic alkylation, adding butene to *iso*-butane at 0–30° C. in the presence of 90–100% sulphuric acid. *neo*-Hexane, however, is best prepared by thermal alkylation, using *iso*butane and ethene as charging stocks.

Another catalytic process of great importance is isomerization, especially of butane to *iso*butane for use in the preparation of *iso*-octanes, but also generally of *n*- to *iso*paraffins.

The development of catalytic dehydrogenation of gaseous paraffins to olefines and hydrogen gives an immense source of raw materials for the synthesis of chemical derivatives, including synthetic rubber. By catalytic cyclization of the lower-boiling members of paraffinic crudes, a new source of aromatics is available for the explosives industry.

Summarizing, the author concludes that, from its petroleum sources, the U.S.A. is more than self-supporting in gasolines up to and surpassing 100 octane number; it could produce billions of pounds of explosives, and it could be more than self-supporting in synthetic rubber. T. T. D.

390.* High Gasoline Yield by Polyform Process. P. Ostergaard and E. R. Smoley. *Oil Gas J.*, 2.9.40, **39** (18), 52.—The basic principles of the polyform process and operating data based on five plants in operation are discussed in detail. The polyform process consists of processing a cracking stock mixed with gaseous hydrocarbons at higher temperatures and at a higher degree of conversion per pass than is possible under normal cracking conditions, without excessive coke formation. Polymerization and other side reactions increase the yield and give more valuable products.

In normal cracking below the critical temperature of the oil a film of the latter forms on the furnace tubes, preventing the stock being cracked to a more severe degree than if the oil alone were present. The introduction of sufficient gaseous hydrocarbons increases the critical temperature of the mixture to that at which the oil can be cracked by itself. At this point the film on the tube wall is of the same composition as the main body of hydrocarbon vapour passing through the tube. From a knowledge of the properties of the cracking stock the optimum quantities of C_3 and C_4 hydrocarbons which must be recycled through the coils can be calculated.

East Venezuelan naphtha, West Texas gasoline, and a 50/50 blend of M.C. and Pa. gasoline gave yields on polyforming in a simple once through unit of 77–84% of cracked distillate which when stabilized had an O.N. of 75–76. Typical operating conditions were: back pressure on heating element 1000–1500 lb. per sq. in., tower pressure 300–400 lb., and outlet temperature from heater 1020–1125° F.

Two polyform units are equipped with coking drums which handle the polyformed residue, utilizing the waste heat in the furnace discharge, producing in addition gasoline and gas oil suitable for thermal cracking.

A two-coil and a four-coil combination crude polyform unit are in operation, the latter producing from crude oil only straight-run gasoline, polyformed distillate, C grade fuel oil and dry gas.

In naphtha polyforming it is always possible to produce a 75–77 O.N. gasoline from any stock, the spread between A.S.T.M. Research O.N. being 9–14, as compared with 5–9 for thermal-cracked gasoline. The road octane numbers also show a higher appreciation. Blending value is high (87–110), and lead susceptibility similar to that of thermally cracked gasolines. Treating presents no difficulties, inhibiting only being necessary for incorporation into coloured blends and clay treatment for production of water-white blends. By modifying conditions, a distillate of 80–84 O.N. can be produced, which on acid treatment gives aviation of 77–79 O.N. requiring less than 3 c.c. lead to give 90 O.N., and an 80 O.N. aviation safety fuel. Such distillates contain high percentages of toluene and zylene, which can be concentrated by distillation. C. L. G.

Hydrogenation.

391.* Destructive Hydrogenation Improves Product from Inferior Hydrocarbons. R. Fussteig. *Petrol. Engr*, March 1940, 56–62.—In the petroleum industry, hydrogenation implies destructive hydrogenation, with the intention of increasing the yield of high-grade gasoline from crude. It is thus pyrolysis followed immediately by addition of hydrogen. Hence the free radicals formed when the charge stock is decomposed are stabilized instead of being allowed to interact and form unwanted polymers of low H-content such as coke and tars.

In order to obtain the best yield of gasoline, the most suitable catalyst must be used in both cracking and hydrogenation processes, the first to increase cracking velocity so that the formation of gaseous hydrocarbons is at a minimum, the second to bring about hydrogenation before polymerization can take place.

Early research was hindered through the poisoning of catalysts by the hetero-elements present in petroleum, and even with the modern non-poisonable types difficulties are still encountered. For instance, with heavy oils, except at low throughput and partial pressure of products, the catalyst tends to be inactivated by the charge stock itself. To obviate this difficulty, the process is divided into two stages, liquid phase and vapour phase, each with its appropriate catalyst. In the first process higher molecular-weight hydrocarbons are split and hydrogenated to middle molecular-weight hydrocarbons, which, in turn, are split and hydrogenated in the vapour-phase process. In the hydrogenation of coal or charcoal a three-stage process must be employed for maximum efficiency: first the oil–coal paste is hydrogenated in the "liquid" phase to produce a heavy oil, which is once more hydrogenated in the liquid phase and finally in the vapour phase.

Besides the true destructive hydrogenation processes, there are in existence combined hydrogen-addition-cracking systems which differ in that simultaneous decomposition and hydrogenation take place in the former, whereas in the latter the hydrogenation takes place after the rearrangement of the hydrocarbon vapour.

The author concludes with descriptions of the flow-sheets of three existing hydrogenation plants, two using heavy oils as charge stock, and the third coal.

T. T. D.

392. Patent on Hydrogenation. H. B. Kipper. U.S.P. 2,224,603, 10.12.40. Appl. 17.8.39. Dehydrogenation and oxidation of petroleum oils to produce so-called drying oils. The oils are selectively oxidized under agitation with nitric acid in the presence of an oxide of a metallic element, as a catalytic material. Thereafter the oxidized oils are condensed with resins in the presence of so-called solid phosphoric acid.

H. B. M.

Polymerization and Alkylation.

393. Patents on Polymerization and Alkylation. P. H. Sykes. E.P. 530,642, 17.12.40. Appl. 16.6.39. Process for the production of solid polymers of *iso*butylene by passing *iso*butane over a dehydrogenating catalyst, cooling the resulting gases to condense liquid *iso*butylene and any unchanged *iso*butane, and polymerizing the *iso*butylene in the liquid condensate, in the presence of an inorganic halide polymerizing catalyst at a temperature below −7° C.

Les Usines de Melle. E.P. 532,158, 17.1.41. Appl. 16.9.38. Catalytic polymerization of diolefines in which a peroxide of tetrohydrofurfurane, or its homologues, is used as a catalyst.

Universal Oil Products Company. E.P. 532,381, 23.1.41. Appl. 19.5.39. Catalytic polymerization of normally gaseous olefinic hydrocarbons consisting substantially of propylene and/or butylenes to form olefinic polymers of gasolene boiling range.

Anglo-Iranian Oil Co., E.P. 532,864, 3.2.41. Appl. 26.4.39. Continuous process for the alkylation of *iso*butane or *iso*pentane by condensation with one or more of the reactive olefines specified. The catalytic contact agent and the *iso*paraffin are together circulated in a stream in a number of successive reaction stages at a rate in considerable excess of the rate of addition of the olefin to the stream, and at a considerably higher rate than the proportional feed rates of *iso*paraffin to total olefine to the stream. Thus under the intensive conditions of turbulence of the stream a low maximum content of olefine is maintained in the stream in the course of the reaction in the stages.

A. L. Blount. U.S.P. 2,225,544, 17.12.40. Appl. 14.5.38. Process for the manufacture of alkylated *iso*paraffinic hydrocarbons. *iso*Paraffinic hydrocarbons having less than 7 carbon atoms per molecule are reacted with olefinic hydrocarbons having more than 2 carbon atoms per molecule, in the presence of a catalyst containing strong sulphuric acid, a dehydrating agent, other than the alkylating catalyst, which is compatible with the said catalyst.

H. B. M.

Refining and Refinery Plant.

394.* Progress in Refining of Crude Petroleum. A. L. Foster. *Petrol. Engr*, Midyear 1940, **11** (10), 28–34.—Trends of refining progress in 1939 have been in the direction of increased specialization in personnel, process, and product. The first is shown by the much greater use of technical graduates not only in the research and development departments, but also in the operating and maintenance divisions. This trend can also be seen in the wider use of pilot plants and semi-plant scale units designed to bridge the gap between test-tube scale laboratory operations and the full-scale operation of the commercial plant that must be economically profitable.

In the field of process development the control of plant processing in the light of product requirements was particularly outstanding in 1939. More than ever, the processes used by the refiner determine the properties the product will exhibit, and bearing in mind the qualities demanded by competition and by the consumers' needs, the refiner works to produce the product required. Of the processes which have recently come to the fore, the most important are catalytic polymerization and alkylation, especially the latter. In this process an olefine is combined with a normal paraffin to form an *iso*paraffin in the motor- and aviation-fuel boiling ranges. Sulphuric acid is the most general catalyst, but others may soon be brought into commercial use. In combination with these two processes, catalytic dehydrogenation of paraffins to the corresponding olefines is carried out on a large scale, using oxides of Al, Ni, Cr, Fe, and V as catalysts.

Thermal dehydrogenation and alkylation are also processes in use commercially, a most important example being the thermal dehydrogenation of ethane to ethylene and its addition to *iso*butane to yield *neo*-hexane—a volatile high-octane-number constituent of 100 octane fuels. Less well developed are processes of isomerization for converting *n*-paraffins into the much more desirable *iso*paraffins, cyclization of chain hydrocarbons to the corresponding *cyclo*-compounds, and aromatization in which the final products are benzene, toluene, ethylbenzene, etc.

In the refining of light distillates, treated bauxite is used as a catalyst for removing mercaptans, sulphides, and disulphides, although thiophenes are not removed. Advantages of this method are a slight increase in octane number of the distillate itself, and a considerable improvement in the lead susceptibility.

In the processing of lubricating fractions, physical and chemical methods have been confined almost entirely to solvent extraction for removal of naphthenic, aromatic, and other undesirable fractions, and for removal of wax. The technique of filtration has also progressed with the introduction of new filter media and improvement of older products and methods.

Addition agents are coming into wider use either as oxidation inhibitors or as detergents for oil-oxidation products. Inhibitors include many N, S, halogen, and organic derivatives of both inorganic and organic elements and compounds. Detergents include, besides soaps and esters, substituted organic materials, both aliphatic and aromatic.

In the development of new products, many types of material are now synthesized commercially from petroleum. Solvents, alcohols, resins, plastics, synthetic rubbers, including butyl rubber and buna, are all derived from materials of petroleum origin, frequently beginning with olefines or *iso*paraffins as raw material. So great are the possibilities of developments of this nature, that there is no doubt that synthesis will become one of the most important branches of the petroleum industry. T. T. D.

395.* Stabilization Process of Natural Gasoline Extraction. R. W. Machen. *Petrol. Engr*, March 1940, 83–86.—The author describes in general terms a typical plant for the separation of natural gasoline into motor spirit and liquid gases. The system consists of a fractionating column of " bubble-cap " type having 26–40 plates in conjunction with conventional heat exchangers, reboiler or kettle, reflux coolers and condensers, temperature controls, back-pressure regulators, liquid-level controls, feed and reflux pumps. The raw gasoline enters the column where the vapour pressure of the tray liquid is equal to that of the hot charge, the stabilized gasoline is run off from the bottom of the column, and the liquid gases from the top. T. T. D.

396.* Water-Wash and Heat Reduce Salt Content 96%. Anon. *Refiner*, February 1941, **20** (2), 43–44.—Water-wash, heat, and settling are used to solve the problem of desalting crude oil in one plant. Despite treating on leases in Eastern New Mexico, crude oil from the Mescalero sand area comes to the plant with as much as 150 lb. of salt/1000 brl. in winter and 50 lb./1000 brl. in summer.

The process, adopted after limited success with previous methods, reduces the salt content to 4·5 lb./1000 brl. in winter and as low as 2·5 lb./1000 brl. in summer. In addition to salt removal, the treating process allows sand and other solids to settle out, a process which is stimulated, since heat is a part of the process.

The treating plant consists of two horizontal settling tanks, three shell-and-tube heat exchangers, a steam coil, and a mixing nozzle. It functions ahead of the topping plant.

The operation of the plant is described. A. H. N.

397.* Further Improvements in Drum Construction. Anon. *Chem. Met. Eng.*, June 1940, **47** (6), 406–409.—Because of the convenience and attractive savings possible for the consumer through use of the new single-trip container over the returnable type, its adoption by the alcohol, solvent, paint, and petroleum industries was immediate, and an estimated annual production of 6,000,000 drums was attained by 1938. Certain faults were found, and the correction of these faults and the development of a newer and improved type drum are the subject of the paper. This type is the I.C.C. 5E. drum with 20-gauge sidewall.

A test programme in studying the new type drum included the following: (1) physical and chemical characteristics of the steels used, and fabricating techniques; (2) effect of yield-point of steel on the stability of swedged-out rolling hoops; (3) effect of yield-point on resistance to denting and weaving; (4) service tests to compare the 20-gauge I.C.C. 5E. drum of stiff steel with the all 18-gauge I.C.C. 5E. drum fabricated from ordinary soft steels. The test programme was inaugurated during October 1938, and extended over a period of a year. The tests are described, and the results are illustrated by photographs. Results are favourable.

In developing the drum as a single-trip container it was intended to be used primarily for hazardous liquids of low specific gravity, such as alcohol and various solvents. This drum should not be overloaded, and the committee has recommended that the maximum nett weight of contents shipped therein should not exceed 450 lb. Better-quality sheet steel is now available, and improvements in design and fabrication have been made. It is expected that the I.C.C. 5E. drum with 20-gauge sidewall will be even more extensively used in the future. A. H. N.

398.* A New Heat-Transfer Medium. W. E. Kirst, W. M. Nagle, and J. B. Castner. *Chem. Met. Eng.*, July 1940, **47** (7), 472–475.—A molten mixture of nitrates and nitrites of sodium and potassium, known as HTS, has recently come into large plant-scale use as a heating and cooling liquid. This mixture, which consists of approximately 40% $NaNO_2$, 7% $NaNO_3$, and 53% KNO_3, by weight, has been adopted because it has a low melting point, a high heat transfer rate and a thermal stability, and a lack of corrosive action on steel at temperatures above those obtainable with Dowtherm, hot oil, or steam.

While similar nitrite and nitrate mixtures have been employed for a great many years in molten baths for the heat treatment of metals and in small installations requiring heat removal at a high temperature level, their use as heat-transfer salts on a large scale began with the installation of the Houdry units for the catalytic cracking and refining of petroleum.

Heat-transfer characteristics of steam, mercury, molten lead, and a patent salt mixture called " NS " are discussed. Hot oil, Dowtherm, and HTS are the principal commercial heat-transfer fluids now available for installations in which the temperature of steam is insufficient and in which flue gas is inapplicable, for any reason. The practical top limit for oil is somewhat over 550° F., and that for Dowtherm is approximately 700° F., above which temperatures these organic materials begin to coke and plug up pipe-lines. The upper practical limit for HTS has not been established definitely. At present it appears to lie in the range between 900° and 1100° F. depending on operating conditions and economic factors. The salt mixture can be used as a heating or cooling fluid at atmospheric pressure and at temperatures that are 200–400° F. higher than the top limit for Dowtherm.

Properties of HTS are detailed, with graphs giving the variation of such properties as density, viscosity, and heat-transfer coefficients under different conditions. Further, the stability, corrosion effects, safety precautions, and explosibility are all discussed.

A. H. N.

399.* New Trends in Boiler Feed-Water Treatment. F. G. Straub. *Chem. Met. Eng.*, July 1940, **47** (7), 477–479.—The most common classification of boiler feed-water problems is (1) scale, (2) corrosion, (3) embrittlement, and (4) carry-over. The first two difficulties may be experienced at all points in the water-stream cycle of the power plant, whereas the last two occur only in the steam boiler. There are many methods of boiler-water treatment which prove suitable for one or all of these problems. However, the methods of attack may be roughly classified as treatments used internal or external to the boiler. In the more recent years it has proved advisable to use a combination of both the external and internal treatments. These treatments are discussed.

The corrosion most commonly experienced in the power-plant has resulted from dissolved oxygen. The modern plants have resorted to every method available for the removal of the oxygen from the water prior to entering the boiler feed-lines. This has resulted in almost universal chemical treatment being resorted to for the elimination of the last trace of oxygen left after deaeration. Chemicals such as iron, ferrous hydroxide, sodium sulphite, and various organic materials are being extensively used.

Embrittlement in steam boilers results in the failure of the steel in the riveted areas and the areas in the vicinity of the rolled tube-ends. This failure has been attributed to the action of the sodium hydroxide in the boiler-water concentrating in the capillary spaces present in these areas and attacking the highly stressed boiler metal, with the resultant cracking of the steel. Methods of chemical treatment have been worked out whereby the embrittling action of the water may be stopped. This has involved the maintenance of definite amounts of sulphates and chlorides or organic material in the lower-pressure boilers and the reducing of the silica content in the higher-pressure boilers.

Washing steam with feed-water, to reduce the total solids carried over by the steam, and thus to reduce difficulties in the form of turbine-blade deposits, forms the concluding part of the review. A. H. N.

400.* Petroleum Toluol. Anon. *Chem. Met. Eng.*, August 1940, **47** (8), 535–537.—The oldest method of obtaining toluol from petroleum consists of fractionation—generally followed by chemical or physical extraction—of certain crudes. A cut of relatively narrow boiling range containing the toluol (b.pt., 231° F.) is taken from the crude. Subsequently a high degree of fractionation or extraction with some such solvent as liquid SO_2, or a combination of fractionation and extraction, yields toluol of the required purity. This process is of limited application. The production of crudes containing appreciable quantities of toluol is quite limited. No comprehensive study of American crudes with respect to toluol content is available.

It is noted that even if a " toluene fraction " of a naphtha were entirely toluene, and if a naphtha containing 6% of this fraction constituted 30% of the crude, the toluene content of the crude would be only 1·8%.

To obtain more toluol for T.N.T. purposes other means are necessary. One promising method is that for which the groundwork was laid during world War I—low-pressure, high-temperature cracking of petroleum oils. There is some evidence that the characteristics of the oils do not play as vital a part in the yields of toluene as do the conditions under which cracking is carried out. Details of cracking processes are given.

A third means of producing toluol exists in the thermal pyrolysis of hydrocarbon gases from petroleum, such as natural gas and the cracked gases made in refineries as by-products. As in the cracking of liquid feed-stocks, the reactions of the process are complex, and result in considerable amounts of olefines and aromatics.

The production of toluol by the catalytic aromatization of *n*-heptane is another process which is receiving consideration. Normal heptane occurs in many crudes, and may be separated therefrom by fractionation. Toluol is then made by cyclization with dehydrogenation. Synthetic methods using chromic oxide catalysts are briefly mentioned. Another process that is believed to yield large quantities of aromatics although there has been no published account of it, is the so-called hydro-forming process. The principal function of the process, however, is to produce high-octane motor and aviation fuels. A. H. N.

401.* Economy in Tube Grouping in Round-Shell Exchangers. Z. G. Deutsch. *Chem. Met. Eng.*, August 1940, **47** (8), 538–540.—The general requirement of the tube-sheet itself, outside the elementary one of strength to resist bursting pressure or vacuum collapse, is to support the tubes with a tight, maintenance-free joint. When the fluids separated by the tube surfaces of a heat exchanger have nearly the same density and specific heat, the cross-sectional areas should be as nearly alike as possible. This is not invariably true, but frequently so in the author's practical experience. For such problems the best approach to "theoretical" economy of materials is obtained by using the smallest tube diameter, the longest tubes, the closest possible tube spacing, the thinnest possible tube walls that can be justified.

The paper discusses further the arrangements of tubes in the shell, and two typical arrangements are shown to be preferable to the other two studied. Tables and charts are given so that designers can utilize them in arriving at an economical number of tubes and a preferable arrangement of such a number of tubes to any other.

The data in this paper have been computed only up to about 120 tubes. With larger numbers of tubes there is relatively less difference in area ratio. Also, in working with larger tube bundles the designer is generally faced with circumstances which make the use of a perfectly symmetrical bundle less and less likely. This is because it is necessary to accommodate certain nozzles, connections, circulating pipes, etc., which interfere with the uniform placement of tubes across the entire cross-sectional area of the shell. A. H. N.

402.* Gulf Introduces New Petroleum Refining Process. Anon. *Chem. Met. Eng.*, September 1940, **47** (9), 626.—The polyform process differs from thermal cracking in that the oil is processed in admixture with normally gaseous hydrocarbons, particularly propane and butane, at higher temperatures and pressures. The result is a higher degree of conversion/pass, with a consequent increase in yield and octane number.

The theory of the process is that, in addition to the normal cracking of long hydrocarbon molecules which is obtained at these high temperatures and pressures (about 1000° F. and 1000 lb./sq. in.), a certain amount of polymerization of the C_3 and C_4 hydrocarbons will occur. Also the introduction of the gases cuts down coke formation, allowing the unit to operate at higher temperatures, with the consequent increase in conversion/pass.

The principle of the process is that the charge to the furnace must be one continuous phase. Normally, the liquid phase tends to be suspended in the vapour phase (largely the gaseous additives) in the form of minute droplets. These are thrown out against the tube wall, forming a thin oil film. Heat transmitted through the tube wall must pass through this oil film, which therefore determines the coking characteristics of the tube. In order to produce a continuous vapour phase, the proportion of light hydrocarbons must be increased to a point where the critical temperature of the mixture is reduced to the temperature of operation. This does away with the oil film, substituting a vapour film, which is less susceptible to coking.

Details of a typical plant are given. A. H. N.

403.* Notes on the Design and Operation of a High-Temperature Dowtherm System. R. E. Hulme. *Chem. Met. Eng.*, October 1940, **47** (10), 685–687.—Dowtherm is the eutectic mixture of diphenyl and diphenyl oxide. Many high-temperature heating processes are now being carried out through the use of indirect heat-transfer media such as Dowtherm. Compared to direct heating, any vapour medium makes possible much closer control, usually with marked improvement in yield and quality of the product. In comparison with steam, however, Dowtherm vapour permits temperatures up to about 700° F. at relatively low jacket pressures, and still without appreciable deterioration of the medium. However, many new problems in design, materials, and technique are thus introduced. Several of these problems of manipulating, maintaining, and controlling Dowtherm systems are discussed. A. H. N.

404.* Safety and Fire Prevention. Anon. *Chem. Met. Eng.*, October 1940, **47** (10), 700–706.—The paper deals with American safety organizations and recommendations. After studying the frequency and severity of various types of accidents and analysing their causes, the following conclusions summarize the findings of the writers.

Chemical industry in 1939 set some enviable records in accident prevention, ranking seventh in frequency and seventeenth in severity among the thirty major injuries charted by the National Safety Council. But there is urgent need for improvement, particularly in the records of fatalities.

Contrary to popular opinion, most accidents in chemical industries are not caused by fumes and flames, but by slips and falls, common tools and machinery—the same as in all other industries. The reason is that the chemical group has learned how to protect itself against chemical hazards, but has failed to conquer some of the common causes of injury.

Accidents annually cost chemical industry approximately $10,000,000, or $40 per worker/year. There are handsome dividends in safety work for those who apply it in the right way.

Fire-prevention practices and equipment have changed to keep pace with the rapid development of new chemical products and processes. Obsolete, antiquated fire-extinguishers and fire-fighting apparatus had best be discarded before it is too late.

Recent chemical engineering graduates have been criticized because of lack of knowledge about industrial hazards and failure to appreciate the vital relation between safety and plant efficiency. Several educational institutions are awakening to the need for training in at least the fundamentals of safety engineering. Others should follow. A. H. N.

405.* Applying Water-Pumping Equipment to Process Pumping Problems. G. L. Montgomery. *Chem. Met. Eng.*, December 1940, **47** (12), 840–843.—A process industry where vertical pumps are finding considerable application for process liquid handling is the petroleum industry. For quick unloading of crude oil or fuel oil from tankers to barges or shore, deep-well turbine pumps are being installed directly on the boats, with the motors above decks and the pumps submerged in the oil compartments of the tanker's hold. This has proved to be an economical and safe unloading method.

In refinery operation, and also in handling such refinery products as gasoline and butane, the vertical pump is finding wide application. For use where the service is hazardous, some pump designers have brought out special pumps in which the motor is submerged in an isolating liquid, so that fire or explosion hazard is minimized.

In pumps of this type the motor, below the pump, and the pump itself are inserted in a heavy cylindrical barrel and suspended from the flanged barrel cover. The motor runs in oil, and a mercury seal prevents the pumped liquid from entering the motor. The lower part of the barrel, surrounding the submersible motor, is filled with an isolating liquid that is immiscible with the liquid being pumped. This prevents the possibility of the motor igniting any flammable liquid that the pump handles. The liquid enters a suction nozzle at the top of the barrel and floats on the isolating liquid. Pump discharge is through the top of the barrel. Examples of vertical centrifugal pumps in refinery works are given.

One distinct advance made in recent years is the development by almost all pump-makers of types of small, standard centrifugal pumps in which the motor and pump are built together as a unit, often with the motor mounted directly on the pump-casing or vice versa. With such pumping units the assembly can be mounted in any convenient position, with the shaft horizontal, vertical, or at an angle. This is a great help in making installations in crowded locations or directly on the equipment served by the pump.

Where positive delivery in exact quantities is in demand for process work, the rotary pump continues to give excellent service. An example is given of seven rotary pumps in a lubricating-oil blending plant. A. H. N.

406.* South African Materials as Substitutes for Imported Earths in Connection with Oil Refining. G. A. Smith. *J. Chem. Met. and Min. Soc. S. Africa*, 1940, **41**, 197–208.—An investigation into the possibility of finding South-African-produced substitutes for lubricating-oil refining earth is detailed. Normally such material would be fuller's earth, bentonites, bauxite, silica gel, or carbon. Bauxite and bentonites are not available in South Africa, and silica gel is not considered to be very efficient for lubricating-oil refinement. The investigation was therefore mainly concerned with the little fuller's earth which was available, with carbon and with two unusual possibilities —namely, vermiculite, a form of mica, and magnesite or naturally occurring magnesium carbonate.

The improvement in colour when a used lubricating oil is agitated for a standard time at 150° C. was utilized to assess the efficiency of each of the materials used.

An active form of magnesium oxide was prepared by calcining magnesite at 700° C. Although slightly inferior to recognized treating earths in decolorizing ability, the active magnesia produced at least as stable a regenerated oil, judged by British Air Ministry oxidation tests, etc., as a highly active bentonite. The filtration rate of the magnesia-treated oil is slow, but can be improved by the addition of diatomaceous earth. The latter increases the porosity of the magnesia slime pad formed during filtration.

The temperature of calcining the magnesite is critical, and heating above 700° C. reduces the activity of the product. Particle size must be less than 200 B.S.S. mesh. The production cost of the magnesia in South Africa is calculated to be ½*d.* per lb. Imported earth costs 5½*d.* per lb.

Attention is directed to a method of preparing active magnesia by the lime precipitation and subsequent calcination of magnesium hydroxide from sea-water.

Fine-mesh active carbon produced from South African coal was found to have extremely good oil-refining properties.

Exfoliated vermiculite, which, because of its very large surface area, was expected to be very efficient, was, in fact, very disappointing. Its failure is attributed to lack of the " capillary pores " which in an active material absorb the colouring matter in oil.

The attempt to find a suitable South African clay was not successful. A partly active clay was produced in the Riversdale district, and the activity of this was improved by acid-washing to remove carbonates, but the results were not impressive, and it was concluded that South Africa does not possess any natural treating clays.

During the work it was demonstrated that there is no correlation between the malachite-green absorptive power of a clay and its decolorizing ability. T. C. G. T.

407.* Slurry-Type Copper Chloride Treater. F. A. Deering, *Oil Gas J.*, 5.9.40, **39** (17), 43.—Hypochlorite treatment of stabilized light straight-run mixed with cracked gasoline has been replaced at an Arkansas City refinery by treatment with a slurry of 200-mesh fuller's earth and copper chloride. The gasoline is caustic washed, dehydrated in a salt tower, steam heated and passed to the base of the slurry tower. Before the tower, an eductor leads oxygen (averaging ½ cu. ft. per brl., but depending on the mercaptan content) into the stream. The stream leaving the slurry tower is water-washed, and scrubbed with water and passed into a further salt tower. The final product is doctor sweet, clear, and bright. A blend of 20% copper-treated stock and 80% cracked gasoline requires 12% less tetra-ethyl lead than when using hypochlorite, whilst the induction period is approximately 30 min. longer. C. L. G.

408. Patents on Refining and Refinery Plant. W. W. Groves. E.P. 531,120, 30.12.40. Appl. 12.7.39. Improvement in the process of dewaxing hydrocarbon oils, such as mineral oils, tars, etc., in which the oil is diluted with a mixture of liquid sulphur dioxide and an auxiliary solvent which increases the solvent power of the sulphur dioxide. According to the invention, the oil to be dewaxed is passed after dilution into chillers having scraping devices and constructed as double pipe-chillers in countercurrent to cold liquid sulphur dioxide.

C. H. Leach. E.P. 532,604, 28.1.41. Appl. 11.9.39. Design of a heat-exchange apparatus intended particularly for use in refining petroleum oil. The apparatus comprises a fixed head, a plurality of floating heads spaced from the fixed head, heat-exchange tubes connected between the fixed and floating heads to form a fluid passage, a shell enclosing the tubes and floating heads, and a baffle inside the shell for forming a vapour passage.

Standard Oil Development Company. E.P. 532,792, 30.1.41. Appl. 20.8.39. Method of separation of a hydrocarbon fraction of the class of naphtha, kerosine, and light gas-oil into its relatively more paraffinic and relatively more aromatic constituents. The hydrocarbon fraction is separated with tetraethylene glycol.

R. E. Burk and E. C. Hughes. U.S.P. 2,225,546, 17.12.40. Appl. 31.12.37. Process for dewaxing oils by subjecting them to the action of butylamine, chilling, and separating the wax.

B. Hopper. U.S.P. 2,227,089, 31.12.40. Appl. 7.2.38. Stabilization of oil treated with a copper reagent in the presence of oxygen. The copper-sweetened oil is treated with a carbonate of a metal above hydrogen in the electro-chemical series.

D. W. Mapes and E. M. Dons. U.S.P. 2,227,377, 31.12.40. Appl. 23.9.38. Prevention of oxidation in using propane and acid to refine lubricating oils. A lubricating-oil stock is dissolved in liquid propane, treated with sulphuric acid, and the sludge removed. Thereafter finely divided neutralizing earth is mixed with the solution of acid-oil and propane, and finally the propane is distilled from the oil.

W. F. Houghton. U.S.P. 2,229,209, 21.1.41. Appl. 19.8.38. Method of separating hydrocarbon oil containing paraffinic and naphthenic constituents into a plurality of fractions of progressively increasing paraffinicity. H. B. M.

Synthetic Products.

409.* Rubber from Petroleum Gases. D. North. *Chem. Met. Eng.*, April 1940, **47** (4), 220–224.—All commercial synthetic rubbers are produced, in part at least, from one or from either one of two of the following unsaturated hydrocarbon gases : butadiene, *iso*butylene, acetylene, or ethylene, which are derived from petroleum, coal, or, as with butadiene in Russia, from vegetable sources. Buna rubber is derived from butadiene, obtained in Germany from acetylene ex carbide, or more recently from hydrocarbon gases of synthetic petroleum production, and in the United States from petroleum gases. *iso*Butylene is obtained from petroleum gases. Neoprene is derived from acetylene, Thiokol from ethylene, and vinyl chloride from either acetylene or ethylene.

Immense strides also have been made in " rubbers " derived primarily from materials other than petroleum gases, notably neoprene, Thiokol (one raw material comes from cracked hydrocarbons), and the polymerized vinyl chlorides in the United States and " Sovprene " in Russia. Neoprene is derived by catalytic synthesis of acetylene to monovinylacetylene, and reaction of hydrogen chloride on the latter to form chloroprene. Chloroprene is then polymerized to the rubber-like material neoprene. Excellent resistance to animal, vegetable, and mineral oils, to sunlight, heat, ozone, and most chemicals has led to widespread use of neoprene in gasoline and oil hose, protective clothing, footwear, packing, and gasket material, protective coverings for wires and cables, and many other uses.

Similarly, other synthetic rubbers are described and their manufacture is outlined briefly. Butadiene rubbers are treated in greater detail than the others. The process of purifying butadiene consists of the formation of the temporary derivative butadiene-sulphone from which a resultant butadiene product of over 99·5% purity is obtained. Its superiority over German butadiene is indicated in that an atmosphere of nitrogen is unnecessary for polymerization to synthetic rubber, as with the German product.

The best grades of butadiene rubbers are resistant to animal, vegetable, and mineral oils, but swell in aromatic hydrocarbons, ketones, alcohols, and esters, and in chlorinated hydrocarbons and organic bases they swell more than natural rubber. In ageing, exposure to sunlight, in resistance to heat, ozone, moisture, abrasion, and flexing, in permanent set and creep, and in hysteresis loss, they are superior to natural rubber. The potential supplies of butadiene are enormous.

Rubbers produced from *iso*butylenes are discussed from the viewpoints of properties and utility. The four principal outlets for these rubbers from *iso*butylene are in compounding of lubricating oils, in various modifications of paraffin wax such as Parofilm, in rubber compounding, and in the manufacture of adhesives such as tin pastes, paper-backed metal foil, facing of bottle cap-liners, and heat-sealing compounds. A. H. N.

410.* Synthetic Glycerine from Petroleum. E. C. Williams. *Chem. Met. Eng.*, December 1940, **47** (12), 834–838.—Synthetic glycerine may be obtained from carbon monoxide and hydrogen. This process involves the condensation of carbon monoxide with formaldehyde to give glycolic acid, reaction of this with a formal, and ultimately the alcoholysis of a formaldehyde derivative of glycerine.

Of the numerous syntheses possible, however, the most direct are those starting with the three-carbon skeleton. This is particularly so when petroleum is to be made the ultimate starting material, since unlimited amounts of propylene and propane are available from this source. Even when these limitations are made, the possible syntheses are legion. Thousands of investigations were necessary to determine which one might have the best commercial possibilities. A line of synthesis starting with propylene and proceeding to allyl chloride to allyl alcohol (or to glycerine dichlorohydrin) to glycerin was finally chosen. The step-by-step development of this process is described in the order of the compounds mentioned. It is emphasized that the discovery of the " hot chlorination " of propylene made the process feasible, also a larger-scale plant might not use the allyl alcohol step.

The glycerine hydrolysate is concentrated in much the same way as soap glycerine lyes, and then vacuum distilled. This leads to a crude glycerine which does not yet meet commercial specifications. However, by making appropriate cuts during the distillation, extracting with a solvent such as xylene (U.S. Pat. 2,154,930), and redistilling, a glycerine is secured which meets all commercial specifications.

A. H. N.

411.* *neo*Hexane for 100-Octane plus. M. E. Clark. *Chem. Met. Eng.*, April 1940, **47** (4), 225–227.—The prefix *neo* indicates the presence of a carbon atom attached by all four valence bonds to other carbon atoms. Thus *neo*-hexane is 2 : 2-dimethylbutane. Its octane rating is 92 ; its blending properties, however, make it possible to manufacture fuels of 115 octane numbers. This is due to the high lead susceptibility and high volatility of the hydrocarbon. The following are the properties of *neo*-hexane : Reid vapour pressure, 9·5 lb. ; A.P.I. gravity, 84·9° ; A.S.T.M. octane number, 94 ; boiling point, 121·5° F. ; specific gravity, (0·6494) 20/4° C. ; refractive index n_D at 20° C., 1·36887 ; and its freezing point is −144·8° F.

It is produced by thermal alkylation, using ethylene derived from a mixture of paraffin gases by cracking them at 1425° F. and a few lbs./sq. in. above atmospheric, and joining the ethylene with *iso*butane at high temperatures and pressures using excess of *iso*butane. There are a number of products of this reaction which are fractionated. Propane, ethane, and other light materials are eliminated, *iso*butane is recirculated, and *neo*-hexane and other heavy materials are withdrawn and refractionated to yield practically pure *neo*-hexane. A. H. N.

412. Patents on Synthetic Products. U.S. Industrial Alcohol Co. E.P. 531,256, 1.1.41. Appl. 23.6.39. Production of ethylene oxide by passing a gaseous mixture containing ethylene, oxygen, and a non-reactive diluent through a catalyst adapted to promote oxidation of the ethylene at a temperature between 100° and 450° C. at a linear velocity of between 20 and 500 cu. ft. per hour per sq. in. of cross sectional catalyst area.

M. M. Holm, A. L. Lyman, and M. F. Miller. U.S.P. 2,224,349, 10.12.40. Appl. 31.12.34. Production of synthetic hydrocarbon oils of high viscosity index and of higher than 40 sec. Saybolt Universal viscosity at 210° F., and having the properties of viscous liquids rather than of plastic solids.

W. B. Plummer. U.S.P. 2,227,691, 7.1.41. Appl. 29.6.39. Preparation of a synthetic lubricating oil possessing substantially no extreme pressure properties. The composition consists substantially of a synthetic lubricating oil obtained by the condensation of an olefin and about 0·005–0·05% of stably bound sulphur.

H. B. M.

Fire Prevention.

413.* Fire Extinguishers and Fire Hazards in the Chemical Industry. N. C. Jones. *Chem. & Ind.*, 1941, **60**, 113–119.—Practically all known fire-extinguishing media are reviewed. Fire extinguishers as used in the U.S.A. are approved for use only on the type of fire to which the Underwriters Laboratory consider they are adaptable, and in no instance has a fire extinguisher been approved for use on every class of fire. In Great Britain fire extinguishers may be approved by the Fire Officer's Committee, after examination and test by the Board of Trade and other competent authorities.

For handling petroleum fires foam and mechanical foam are excellent. Carbon dioxide, carbon tetrachloride, and methyl bromide are also effective in certain circumstances. Dry chemical compound powder propelled by carbon dioxide is also most effective, and very quick-acting in extinguishing petroleum fires. This latter extinguisher, which is largely employed in the U.S.A., normally uses an inert gas, nitrogen, or carbon dioxide, to propel the dust, which is mainly sodium carbonate. The hand models weigh 26–55 lb., and contain 8–25 lb. of chemical dust. The carbon dioxide is contained in a cartridge, and the pressure is sufficient to blow the compound a distance of over 25 ft. The model holding 25 lb. of compound will handle fires of 150 sq. ft. Portable models having a capacity of 150 or 350 lb. of compound are equipped with nitrogen cylinders which supply sufficient pressure to throw all the compound 50 ft. The advantages of the apparatus are :

1. Simple and dependable.
2. Clean in action and controllable.
3. Unaffected by cold.
4. No damage to materials, plant, or machinery.
5. Effective over wide range.
6. Reasonably cheap.
7. Effective on gas, oil, inflammable liquids, and electrical fires.
8. Can be used in the open or in confined places.
9. Dry powder acts as an absorbent.

The efficiency of this type of extinguisher was illustrated during experiments with oil-incendiary bombs. The residual oil from a paraffin fire which had been extinguished by such means, when re-ignited was not extinguished by foam.

Water, acid and soda, foam, mechanical foam, chemical liquid extinguishers such as carbon tetrachloride and methyl bromide, inert gases, loaded stream (*i.e.*, solution of alkali metal salts), and systems that combine several of these methods, are all outlined and their individual advantages tabulated. The uses and application of heat fuses for automatic systems are outlined, as also are numerous hazards peculiar to special industries. T. C. G. T.

Chemistry and Physics of Petroleum.

414.* Elements of Vaporization and Condensation. Part XI. R. L. Huntington. *Refiner*, February 1941, **20** (2), 47–50.—The paper furnishes illustrative exercises and problems for the subjects treated by the author in the previous ten parts. Differential and flash vaporization as well as fractionator operations are studied.

A. H. N.

415.* Hydrogen Content as a Basis for Correlating the Specific Heat of Liquid Hydrocarbons and Petroleum Fractions. J. Griswold and H. A. Alves. *Refiner*, February 1941, **20** (2), 52–54.—From the assumption that the molecular-heat capacity of a liquid hydrocarbon is the sum of the atomic-heat capacities of its carbon and hydrogen atoms, a linear relation between specific heat at 32° F. and the weight-% hydrogen results applicable to petroleum. The correlation is good between normal paraffin and aromatic hydrocarbons, but not for naphthenes and olefines by this procedure.

Specific-heat data on petroleum fractions for which the hydrogen content could be estimated are obtained from the literature. These and experimental values correlate very nearly as closely as by the best equations hitherto developed, by the equation :

$$(C_p)\ 32^\circ\text{ F.} = 0{\cdot}0152\ (\text{Wt.-\%H}) + 0{\cdot}2448.$$

The data for pure hydrocarbons and for petroleum fractions are given in graphical form. Estimation of hydrogen content is made by means of Watson's correlation of the characterization factor and hydrogen content. Another formula used was :

$$\text{Wt.-\%H} = 14{\cdot}3 + 0{\cdot}175\ (^{\circ}\ \text{A.P.I.}) - 7500^{\circ}Tm.$$

where *Tm* is the mean average boiling point. Experimental work is also described.
A. H. N.

416.* Packed Columns for Close Fractionation. L. B. Bragg. *Refiner*, February 1941, **20** (2), 55–64. *Paper presented before American Institute of Chemical Engineers.*—The packings studied in particular are the Stedman types. The single-cell, conical-type Stedman packing is at present made in three sizes : 0·375-in., 0·750-in., and 25-mm. (0·984-in.) nominal diameters. The multiple-cell, triangular pyramid-type Stedman packing also is made in three round sizes : 2·080-in., 3·080-in., and 6·080-in. diameters. A fourth packing of this type is made having an equilateral triangular cross-section 6 in. on a side, these sections being fitted together to pack columns of hexagonal cross-section. These packings are usually constructed of 40 × 60-mesh wire cloth, using 0·009-in. diameter wire.

The operations of the single-cell and multiple-cell packings are detailed. In the first type reflux liquid flows along the wire cloth and seals the openings of the mesh. The liquid flows out towards the walls of the column on a cone that is concave downwards, and then back towards the centre of the column on a cone that is concave upwards, which is welded to the first cone at the outer edge. The lower cone is welded to another still lower cone at the centre, and the liquid flows through the mesh at the point of junction, then outward towards the walls on this lower cone, and so on until the liquid drops off the lowest cone of the column. The vapour enters the space between two cones, which are welded around the outer edges, through the vapour hole in the lowest cone. The vapour then flows through the space between these two cones, practically at right angles to the axis of the column, and out through the vapour opening in the upper cone of the pair. The vapour then divides and flows around the point where two cones are joined back to back, and across to the side of the column where it first entered the packing. This flow is repeated until the vapour leaves the packing at the top of the column. The working of the multiple cell is similarly detailed.

The packings were tested with mixtures of benzene and ethylene dichloride at total reflux and atmospheric pressure. The data obtained were worked up in the form of column operation factors which permit accurate comparisons between various types of packing and different diameters of columns. Data on other types of columns are included. These data have been converted to be comparable with data on ethylene dichloride mixtures and worked up in the same manner. A. H. N.

417.* Charts Solve Orifice Equations. H. S. Winnicki and R. Koch. *Chem. Met. Eng.*, January 1940, **47** (1), 24.—An alignment chart for the solution of orifice equation for both gas and liquid flow is presented. The ranges of operation are as follows : rate of flow : for liquids from 1–10,000 gals./hr., for gases from 0·001–10,000 cu. ft./min. ; orifice diameter : for liquids 0·1–1 in., for gas 0·07–2·0 in. ; gas temperatures, 400–1000° F. abs., pressure 0·1–250 lb./sq. in. abs. A. H. N.

418.* Vaporization Equilibria. M. Gilbert. *Chem. Met. Eng.*, April 1940, **47** (4), 234.—A chart is presented which may be used in vaporization equilibria calculations on multi-component systems in order to reduce the time necessary to arrive at a solution by trial-and-error methods. The method requires a maximum of three attempts before obtaining an answer. The theory on which the chart is based is derived in the paper for complex mixtures from following Henry's and Raoult's laws, where the vapour pressures lie between those of the pure components.

An illustrative example is solved in detail to make clear the use of the chart.
A. H. N.

419.* Estimation of Unsaturated Hydrocarbons by Bromine Addition. J. S. Green. *J. Inst. Petrol.*, 1941, **27** (208), 68–71.—The bromine number can be used for compara-

tive purposes as a measure of unsaturation in complex hydrocarbon mixtures provided that the conditions of the reaction are precisely specified. An inhibition effect which might be a potential source of error was observed in brominating heptane, nonene, and a benzole fraction by the Francis method, but this did not occur when using the Lewis and Bradstreet titration technique. For the estimation of the actual percentage of unsaturateds, the bromine-absorption method is unreliable unless the molecular weight and type of the olefines present can be determined or estimated with accuracy.
B. M. H. T.

420.* Catalytic Vapour-Phase Oxidation of Aliphatic Kerosine Fraction. W. G. Parks and E. F. Story. *Oil Gas J.*, 5.9.40, **39** (17), 54.—A brief review of the oxidation of kerosine with heterogeneous catalysts is given, followed by detailed results on experimental work on the vapour-phase oxidation of an aliphatic hydrocarbon, C_{12} to C_{14}, fraction from kerosine using homogeneous catalysts—nitric acid vapour and tetraethyl lead. The latter catalyst was preferred owing to the explosive nature of reaction products from the former. With nitric acid vapour the highest yields of aldehydes (20% on the oxidized hydrocarbons) was obtained at 300° C. lengthening reaction time giving higher yields. Acid production (up to 6%) was favoured by lowering temperature and reaction time and increasing the air hydrocarbon ratio. Tetraethyl lead was a more effective catalyst, the optimum results under different conditions being 20% aldehydes and 16% acids.

It is considered that commercial production of these mixed aldehydes and acids with their derivatives is economically possible. Re-circulation of remaining hydrocarbons tended to form acids rather than aldehydes, tetraethyl lead giving traces of alcohols (though none were produced with nitric acid vapour) suggesting that oxidation is by hydroxylation rather than by peroxide formation. Further work is in progress.
C. L. G.

Analysis and Testing.

421. A.S.T.M. Standards 1940 Supplement. Parts II and III. American Society for Testing Materials.—The Supplement to A.S.T.M. Standards, issued for the first time in 1940, contains the new and revised standards and tentative standards adopted since publication of the Book of A.S.T.M. Standards in 1939 and replaces the Book of Tentative Standards.

The Supplement is issued in three parts of which Parts II and III are of principal interest to the petroleum industry.

Part II includes specifications for Asphalt Plank, Cut-Back Asphalt and Quick-Setting Emulsified Asphalt and methods of testing of emulsified asphalts and for water in petroleum products and other bituminous materials.

Part III includes specifications for Gasoline and Stoddard Solvent, and the following new or revised methods of testing: Ramsbottom Carbon Residue, Carbonizable Substances in White Mineral Oil, Distillation of Gasoline, Naphtha, etc., Natural Gasoline and Plant Spray Oils, Dropping Point of Grease, Analysis of Grease. Pensky Martens Closed Flash Point, Gum Stability of Gasoline, Electrical Insulating Oils, Knock Characteristics of Motor Fuel, Precipitation Number of Lubricating Oils, Unsulphonated Residue of Plant Spray Oils, Reid Vapour Pressure, Water Content, Water and Sediment and Calculation of Viscosity Index.

Many of the revisions are of a minor or editorial character, but it should be noted that in the method of test for Ramsbottom Carbon Residue a metal coking bulb has been prescribed in place of the glass bulb and in the Pensky Martens Closed Flash the rate of heating for Cut-Back Asphalts and other viscous materials has been reduced from 4–6° F. per minute to 2–3° F. per minute. A new method for determination of water in grease uses the cone-shaped centrifuge tube as receiver, and this is centrifuged to assist separation of the water and xylol at the end of the distillation, water-free oleic acid is added to the distillation flask as an anti-foaming agent.

The method for determination of dropping point of grease uses the Ubbelohde type of apparatus.
A. O.

422.* Polarographic Determination of Lead in Gasoline. H. A. Frediani and L. A. Bass. *Oil Gas J.*, 26.9.40, **39** (20), 51.—The methods which have been suggested for determining lead in gasolines are listed, and it is stated that the most widely used method is that of Calingaert and Gambrill which involves refluxing the gasoline with HCl and estimating the lead in aqueous solution by a gravimetric or volumetric method.

The authors extract the lead by refluxing with HCl, but determine it in the aqueous solution by a polarographic method. This is considered to save time without sacrificing precision. The dropping mercury electrode is used in this analysis, and it involves current-voltage curves obtained in solutions utilizing a highly polarized cathode and a non-polarizable anode.

Curves are drawn for solutions containing known amounts of lead for comparison with the experimental results. D. L. S.

423.* Identification of Bitumen in Paving Mixtures. A. W. Attwood and D. C. Broome. *Petroleum*, October 1940, **2** (6), 183.—The development of colorimetric methods of identifying bitumens is discussed, and a description given of an apparatus and method of test which has been developed for this purpose. Visual determinations of the colour of bitumen solutions present difficulties owing to varying sensitivity of eyes to the various parts of the spectrum, lack of repeatability, possibility of matching colours by varying combinations of others, and to the fact that standard colour glasses do not transmit light of only that colour. Photo-electric methods are to be preferred, types of instruments available being: (1) the Hirsch Muller, using various vapour-discharge lamps, which is expensive and slow in operation; (2) apparatus consisting of incandescent electric lamps and standard colour filters, and (3) comparometers in which the light from a single lamp passes through two liquid cells connected in opposition. The present investigation resulted in the choice of type 2, the Panchrometer being evolved for the purpose. It consists of a high-intensity light source controlled by a rotary slotted diaphragm, a set of filters covering the spectrum from infra-red to ultra-violet, and a vacuum-type photo-electric bridge connected to a single-stage thermionic valve amplifier. The test is carried out by dissolving the bitumen in benzene to a concentration of 2·5 gm./litre, decanting and centrifuging, placing a 2-mm.-thick cell of the solution in the apparatus and measuring the light transmitted using different colour filters, by the P.D. from the photo-electric cell, the apparatus being first checked against pure benzene. This gives a colour grading of the bitumen throughout the spectrum, which is sufficiently characteristic for the nature of the crude and the approximate penetration to be determined if the corresponding basic figures are known. In addition, the Panchrometer may be used to detect overheating, changes due to ageing and sedimentation from asphaltic cements, and the reaction (adsorption) between bitumen and aggregate.

Colour analyses of a wide range of bitumens are included and a critical survey is made of the available pieces of equipment forming the apparatus. C. L. G.

424.* Testing the Permeability of Asphaltic Surfaces. Anon. *Engineering*, 1941, **151** (3923), 235.—A description is given of a simple type of permeometer consisting essentially of an open cylinder with a base flange faced with a rubber ring. The instrument is held down on the surface to be tested and filled with a measured amount of water, the amount leaking through the surface in a known time giving a measure of the permeability of that surface. B. M. H. T.

425.* Laboratory Oxidation Tests for Lubricants. F. Jostes and A. Hann. *Refiner*, February 1941, **20** (2) 65–69.—The apparent impossibility of obtaining laboratory ageing tests to give concordant results independent of operating conditions and apparatus is discussed and the reasons for the lack of agreement between different types of tests are briefly studied. It is indicated, however, that oils can be compared as to their life or resistance to oxidation when instead of oxidizing them all for the same time period, one employs a method wherein an oil is oxidized until it produces a definite or standard amount of some easily determined end-product, as, for instance, insoluble sludge. Such conditions are obtained by the so-called " Indiana Life Test," which is described as a new and modified procedure of the original Indiana test; this procedure is to use 20 c.c. of oil instead of 300 c.c. as in the original test. Then the oil is also subjected to 650 c.c. of air/hr. at 200° C. The time is then noted which is necessary to produce by oxidation 15 mgm. of insoluble asphalt/gm. of oil.

The testing of ten different oils by the modified Indiana test showed that the sludging time or valuation of these oils is in a wide degree independent of the conditions of temperature and volume of air used.

Several other tests showed that in many cases the viscosity, the acid and saponification values must also be determined, besides the insolubles test. The effect of added oil-resins on the oxidation of an oil is also indicated. A. H. N.

Motor Fuels.

426. Patents on Motor Fuel. A. B. Doran, E. Marston, and K. Walsh. E.P. 532,867, 3.2.41. Appl. 30.5.39. Production of a motor fuel consisting of a hydrocarbon fuel and an anti-detonant comprising an anti-detonant organo-metallic compound of an unsaturated aliphatic hydrocarbon having one metallic atom in the molecule.

H. G. Schneider. U.S.P. 2,225,942, 24.12.40. Appl. 20.11.36. Preparation of a motor fuel consisting of gasoline and di*iso*propyl ketone, the latter component forming 5–50% of the fuel.

J. W. Teter. U.S.P. 2,226,787, 31.12.40. Appl. 14.7.37. Inhibition of oxidation of gasoline by incorporating therein a small proportion of a halogenated saturated cyclic alcohol.

M. M. Holm. U.S.P. 2,228,662, 14.1.41. Appl. 31.5.39. Production of a high anti-knock motor fuel comprising a fuel base consisting essentially of *iso*paraffinic motor fuel hydrocarbons and from 10 to 50% by volume of a saturated aliphatic ester of a monocarboxylic acid.

See also Abstract No. 411. H. B. M.

Lubricants and Lubrication.

427.* Oil Flow Through Engine Bearings. Report of the Automobile Research Committee, prepared by J. Spiers. *Instn. Aut. Engrs. J.*, January 1941, **9** (4) 7–34.—Tests were made on a 6-cyl. water-cooled petrol engine in which the front main and big-end bearings were isolated from the main lubrication system and separate external pumps substituted. Thus the effect of pressure and temperature on oil-flow could be studied. The range of clearances tested was: main bearings 0·0007–0·0055 in., big-end 0·0015–0·005 in. Variable-pressure tests were run at an oil inlet temperature of 70° C., and variable temperature tests at oil pressures corresponding to those given by the engine system under the same conditions. An S.A.E. 50 oil was used mostly, but some tests with small clearance bearings were also run with an S.A.E. 20 oil.

It was found that the rate of oil-flow was directly proportional to the effective oil pressure at the bearing and increased rapidly with speed and clearance. The increased flow at the higher speeds is shown to be due to the reduced viscosity of the oil-film consequent on increased operating temperature; the film temperature varies linearly with speed and is independent of load. The viscosity of the oil at the engine inlet bears little relation to the operating viscosity in the bearing; thus, the increased flow due to changing from S.A.E. 50 to S.A.E. 20 oil was not in proportion to the change in viscosity at the oil inlet temperature, since the operating temperature within the bearing was reduced with the lighter oil.

It is concluded that the flow of oil through engine bearings under operating conditions obeys laws approximating to those of viscous flow through an annular passage. The main factors are supply pressure, viscosity of the oil-film in the bearing and diametral clearance, although other design features will modify the total flow through the bearing. K. A.

428.* Use of Additives in Automotive Lubricants. F. L. Miller, W. C. Winning, and J. F. Kunc. *Refiner*, February 1941, **20** (2), 35. *Paper presented before American Chemical Society.*—After a general discussion on the need for using additives in lubricants, it is indicated that the principal properties which determine the suitability of petroleum oils for the lubrication of engines may be considered essentially to be: (1) viscosity and volatility; (2) viscosity-temperatures and low-temperature flow characteristics; (3) chemical stability; (4) detergent and sludge-dispersing ability; and (5) oiliness and wear characteristics.

The relative importance of these different characteristics, and the degree to which they can be modified by the use of proper additives, form the basis of this paper.

By the choice of proper crudes and by suitable selective refining, motor oils of 80–100 and even 110 V.I. can be prepared economically. It is not practical to obtain higher viscosity indices by these methods except in special cases. On the other hand, it has been found possible in recent years to improve the viscosity index materially through the use of relatively small quantities, in the order of 1–5%, of certain types of high-molecular-weight polymeric linear chain compounds, and premium-quality motor lubricants are now being made successfully by such means.

To counteract low-temperature flow troubles due to wax, pour depressants are used. The pour depressants appear to act (*a*) to keep the wax crystal small and prevent its growth, and (*b*) to prevent adsorption of the oil on the crystal. Both these functions are typically colloidal, and presumably the effectiveness of the different pour depressants depends largely on their colloidal state and behaviour, particularly at low temperatures. Reference is made to various depressants, and especially to Friedel–Crafts condensation products.

A review of the patent and other pertinent literature reveals that the classes of compounds most commonly advocated as anti-oxidants, bearing corrosion inhibitors, and metal passifiers are: (*a*) various types of phenols, (*b*) certain sulphur-bearing compounds, (*c*) numerous organic phosphites, and (*d*) certain of the amines. In a number of instances combinations of one or more of these types are mentioned. Each class is discussed separately and briefly, giving references to original publications.

Detergents and sludge-dispersing ability are next discussed. The use of fatty oils, soaps, and naphthanates for this purpose is detailed.

Except for one or two marketers who are adding compounds to their motor oils to improve oiliness, and a few others who are presumably incorporating anti-oxidants, which happen also to confer extra oiliness, the use of additives to obtain better lubrication properties has not been very extensive. Materials most frequently employed to increase oiliness and film strength contain groups commonly known as polar groups, such as those containing oxygen or phosphorous, or distinctive reactive chemical elements, such as sulphur or chlorine.

Finally a study is made of what are called " multifunctional additives."

A. H. N.

429.* Rubber in Lube Oils. L. Light. *Petroleum*, September 1940, 176.—Natural rubber and synthetic rubber-like materials have been used in the production of improved lubricating oils either in their original form or after modification. Thus rubber hydrogenated in the presence of a nickel catalyst has been incorporated in spindle oils to give products of increased viscosity.

Poly*iso*butylenes have been recommended for flattening the temperature–viscosity curve of hydrocarbon oils. The initial polymerization of the *iso*butylene was carried out by boron trifluoride and the partly polymerized olefine dissolved in oil and treated with anhydrous $AlCl_3$.

In a recent process both rubber and a polymerized olefine are used to improve a hydrocarbon lubricant, the olefine being treated in the presence of rubber.

D. L. S.

430.* Considerations in Valve Lubrication. G. F. Scherer. *Chem. Met. Eng.*, March 1940, **47** (3), 164–165.—The lubricant used in a lubricated tapered plug-cock performs a number of functions which, in order of importance, may be listed as follows: (1) It affects a plastic seal between the sliding contact surfaces of the valve to prevent leakage of the line fluid and to prevent infiltration of foreign matter between these surfaces; (2) it furnishes a fluid medium for lifting the plug from its seat, both to provide a space for the renewal of the lubricant film and to free the plug from its seat if corroded and frozen together ; (3) it effects easy operation of the valve by lubricating the sliding contact surfaces and reducing the friction between them ; and (4) it provides a protection for these surfaces so that the original surface finish is not marred by corrosion which would increase the turning effort and also permit leakage.

The importance of film thickness, viscosity, adhesiveness, spreading quality, and other characteristics which are desirable in a valve lubricant are indicated.

Besides the conventional mineral oils and soaps used in compounding ordinary cup-greases, many other materials are used in the manufacture of valve lubricants. These include vegetable and animal oils, fats, waxes, asphalts, synthetic oils and waxes, graphite, resins, glycerine, alcohols, and various inert materials sometimes used for fillers. A. H. N.

431.* Chemical-Plant Lubrication. Anon. *Chem. Met. Eng.*, March 1940. **47** (3), 172–178.—The paper is divided into four comparatively distinct parts. The first part deals with the elements of lubrication and explains the need and theory of lubrication by elementary and mechanical concepts of the molecules of the lubricant as spheres separating the jagged surfaces of the parts lubricated.

Part II deals with the properties of lubricants. To select the right lubricant for a given job requires a knowledge of the desirable (and undesirable) properties of lubricants. In this paper the sources of lubricants are discussed—mineral, animal, vegetable and others—together with the outstanding properties of lubricants and the tests for them. Significance of viscosity, viscosity index, demulsibility, carbon residue, flash point and others are included. The tests are very briefly described.

In the third part the application of a lubricant is discussed. Boundary and fluid-film lubrication are studied, and several methods of applying lubricants in practice are described and illustrated. The ideal lubricating device should : (1) form and maintain a satisfactory lubricating film under all conditions of operation ; (2) be economical in operation—feed only enough lubricant to maintain a film while the equipment is in motion—not feed while the equipment is at rest ; (3) be automatic—require very little attention ; (4) protect the lubricant from contamination, dust, dirt, water, etc., (5) carry away heat from bearings by a continuous flow of the lubricant ; (6) be convenient to service with lubricant ; (7) be rugged enough to withstand normal abuse and not readily break or become inoperative ; (8) moreover, installation costs should not be too high in proportion to the benefits to be derived. Storing of lubricants is also discussed in this part.

Part IV deals with chemical factors in lubrication. In this section the use of special lubricants for special cases is discussed. In the handling of viscose rayon, especially in the metering pumps, viscose is the best lubricant. The reason is to avoid contamination of product. Handling hydrogen gas requires special technique, soap and water generally being used for lubrication. Likewise equipment for handling oxides of nitrogen is generally soap-and-water-lubricated, although mineral-oil lubrication has been successfully used in at least one installation. Solvents are quite troublesome, as it is necessary to lubricate with a material that is insoluble, yet has lubricating properties. The petroleum industry has many problems in this respect varying all the way from lube-oil pumps, which are self-lubricating, to gasoline pumps, which are often lubricated with modified castor oils. Other cases are mentioned and general principles are discussed. A. H. N.

432.* Speciality Lubricants. D. M. Considine. *Chem. Met. Eng.*, April 1940, **47** (4), 230–233.—The manufacture of oils and greases which contain chemical compounds to fit them for use in special services is described. The paper, however, deals mainly with processes of one particular company, and not in general.

There are three general types of treatment used in the manufacture of hypoid gear lubricants—namely, (1) lead soap, active sulphur, (2) lead soap, sulphur saponifiable, chlorine compound, and (3) organic sulphur compound, chlorinated organic compound. Processing operations at the plant are segregated into three classes, consisting of the preparation of intermediate chemicals, blending intermediates of their own preparation with those purchased from outside chemical manufacturers to produce concentrates, and manufacture of finished lubricants, inluding special greases, motor oils, and industrial lubricants. Certain of the intermediate chemicals blended in the concentrates are produced from suitable raw materials, whilst others are purchased. The operations are essentially batch, although there are features of some of the equipment which make that particular phase of the processing automatic and continuous.

Preparation of intermediates from the raw materials requires such processing as mixing and reacting at ordinary and elevated temperatures, atmospheric and vacuum distillation, dehydration, washing, and filtering. All intermediates do not require the same treatment, and many items of equipment are designed and installed for the purpose of performing various operations. These operations are described separately.

Intermediate chemicals are blended in exact proportions according to the specifications reached as a conclusion from the research findings and data. The constituents are proportioned by volume and mixed by means of a Lummus–Cornell homogenizer. When solid materials are added to the concentrates they are dissolved in suitable solvents, usually one of the other constituents, and then proportioned just as the other liquids through the electrically driven proportioning pumps. The operations of the homogenizer and pumps are described.

Manufacture of grease in the same plant is detailed. A. H. N.

433. Patents on Lubricants and Lubrication. A. J. Rudge. E.P. 532,953, 4.2.41. Appl. 2.8.39. Preparation of lubricating materials suitable for extreme-pressure lubrication and consisting of thiophosphoryl chloride and a lubricating oil.

J. M. Musselman and H. P. Lankelma. U.S.P. 2,224,368, 10.12.40. Appl. 11.11.37. Preparation of a lubricant comprising a mineral lubricating oil and a small proportion of an alkaloid salt of an organic carboxylic acid of at least six carbon atoms.

K. Frolich. U.S.P. 2,224,541, 10.12.40. Appl. 9.6.39. Preparation of a lubricating composition composed of a viscous hydrocarbon oil and a small amount of a synthetically prepared ester having a boiling point above 150° C. of a cyclic acid and of an alcohol having not more than three hydroxyl groups.

A. J. Morway and F. L. Miller. U.S.P. 2,225,318, 17.12.40. Appl. 26.8.39. Production of a lubricating composition comprising a lubricating-oil base stock and a halogen derivative of a substantially saturated linear aliphatic hydrocarbon compound having a molecular weight above about 800 and containing at least 1% of halogen.

U. B. Bray. U.S.P. 2,225,365, 17.12.40. Appl. 18.1.37. Preparation of a mineral lubricating oil containing approximately 1·25% of freely oil-soluble metal salt of a chlorinated fatty acid. In this way ring- and valve-sticking tendencies are overcome in internal-combustion engines without appreciably increasing the viscosity of the original lubricating oil and without imparting grease-like characteristics to the oil.

U. B. Bray. U.S.P. 2,225,366, 17.12.40. Appl. 2.11.37. Preparation of a lubricant composed of approximately 97% of mineral lubricating oil and between 1% and 2% of oil-soluble soap constituent of organic acid containing 10 or more carbon atoms, and including a film-strength increasing constituent consisting of halogens, sulphur, and phosphorus.

U. B. Bray. U.S.P. 2,225,367, 17.12.40. Appl. 29.4.39. Preparation of a freely liquid lubricating oil in which is incorporated a small quantity of an oil-soluble soap of a synthetic petroleum acid. The proportion of the latter constituent is such that ring- and valve-sticking tendencies in internal-combustion engines are overcome.

S. C. Fulton. U.S.P. 2,225,430, 17.12.40. Appl. 25.6.37. Manufacture of a low-pour-point lubricating oil composed of a blend of a wax-containing petroleum lubricating oil with a minor proportion of a pour-inhibiting agent. The latter is prepared by adding to a refractory distillate from a cracking-process tar boiling above 700° F. about 5% by weight of anhydrous aluminium chloride.

M. B. Chittick. U.S.P. 2,225,684, 24.12.40. Appl. 8.8.33. Production of a solid extreme-pressure lubricant consisting of unsaturated hydrocarbon polymers and a soap.

D. E. Badertscher, F. M. Seger, and W. H. James. U.S.P. 2,226,420, 24.12.40. Appl. 3.10.39. Production of an extreme-pressure lubricant consisting of a hydrocarbon oil and a small proportion of mixed anhydrides of an alkyl thiocarbonic acid and an acid of phosphorus. The mixed anhydrides are obtained by the reaction of a halide of phosphorus with an alkali alkyl thiocarbonate.

E. V. Murphee. U.S.P. 2,227,149, 31.12.40. Appl. 23.12.37. Production of an improved lubricant for internal-combustion engines comprising a lubricating oil and a small amount of a polyvalent metal soap of acids derived from the oxidation of " sweater oil."

M. H. Arveson. U.S.P. 2,227,690, 7.1.41. Appl. 6.10.38. Preparation of a diesel-engine lubricant consisting of a paraffinic lubricating oil having a 90% distillation temperature at about 1 mm. pressure of less than 500° F., and an *iso*-olefin polymer having a 90% distillation temperature at about 1 mm. pressure of about 450–700° F.

E. R. Barnard. U.S.P. 2,227,692, 7.1.41. Appl. 19.12.39. Preparation of a diesel-engine lubricant consisting of a blend of 5–95% of a naphthenic-base mineral oil and 5–95% of an*iso*butylene polymer from which the low-boiling and high-molecular constituents have been removed.

A. W. Lewis. U.S.P. 2,227,908, 7.1.41. Appl. 19.3.37. Lubrication of bearing surfaces comprising alloys having substantially the corrosion susceptibility characterizing cadmium–silver, cadmium–nickel, and copper–lead alloys. A lubricant consisting of a mineral hydrocarbon oil having incorporated therein corrosion inhibiting proportions of a thiodinaphthylamine is applied to the bearing surfaces.

W. L. Steiner. U.S.P. 2,228,219, 7.1.41. Appl. 29.12.39. Preparations of a composition of matter consisting of a major proportion of a lubricant and a minor proportion of a physical solution of elemental sulphur in uncombined form dissolved in a minor proportion of a solvent which is a sulphur solvent, and at the same time is itself soluble in the lubricant.

H. G. Berger, D. E. Badertscher, and F. M. Seger. U.S.P. 2,228,252, 14.1.41. Appl. 28.6.39. Preparation of an extreme-pressure lubricant consisting of a hydrocarbon lubricating oil and a small proportion of a perchloromethyl mercaptan.

J. F. Olin and R. H. Goshorn. U.S.P. 2,228,325, 14.1.41. Appl. 27.7.37. Production of a lubricating composition consisting of a hydrocarbon oil and a small proportion of a trialkylammonium salt of an inorganic hydrohalogenic acid.

B. B. Farrington, J. O. Clayton, and J. T. Rutherford. U.S.P. 2,228,658, 14.1.41. Appl. 21.11.38. Manufacture of a composition of matter consisting of a hydrocarbon lubricating oil and a minor proportion of an alkaline-earth metal salt of a substituted acid of phosphorus containing an organic constituent.

E. W. Gardiner and G. H. Denison. U.S.P. 2,228,661, 14.1.41. Appl. 8.10.38. Preparation of a composition of matter consisting of an oil and from 0·1% to 50% by weight of an alkaline-earth metal phenate dissolved therein.

G. L. Neely and E. W. Gardiner. U.S.P. 2,228,671, 14.1.41. Appl. 25.11.38. Preparation of a lubricant consisting of a hydrocarbon oil, a metal phenate, and from 0·05% to 2% by weight of a salt of a substituted acid of phosphorus containing an organic constituent.

L. C. Brunstrum. U.S.P. 2,229,367, 21.1.41. Appl. 29.4.40. Manufacture of a grease composed of a lubricating oil and a soda soap of hydrogenated fish-oil fatty-acid pitch.

L. C. Brunstrum. U.S.P. 2,229,368, 21.1.41. Appl. 29.4.40. Preparation of a heat-resisting grease consisting of a lubricating oil, soda rosin soap, and soda soap of hydrogenated fish-oil fatty-acid pitch.

W. H. Bahlke and T. H. Rogers. U.S.P. 2,229,485, 21.1.41. Appl. 30.11.39. Method of increasing the sludge stability of a petroleum lubricating oil distillate by mixing therewith, prior to treatment with sulphuric acid, 0·1–5·0% of a heavy uncracked petroleum residue.

See also Abstract No. 425. H. B. M.

Asphalt and Bitumen.

434.* Bituminous Soil Stabilization. W. L. Campbell. *Roy. Engrs. J.*, March 1941, **55**, 89–103.—The main idea underlying soil stabilization is the retention of the moisture content of the soil within such limits as will ensure stability, the latter being determined by (*a*) internal friction, (*b*) cohesion, and (*c*) apparent cohesion. As the measurement of stability the bearing strength of the soil surface is determined by means of a cone penetrometer. (Full details of this test are given in an appendix.) The task of the stabilizer is to impose a limit to the variations that could occur in the soil mass as regards moisture content, by reason of ingress of capillary or ground-water. The bituminous stabilizer should be of such a nature that it can be dispersed throughout the soil-mass in such a way as to form automatically a series of plugs throughout the capillary structure of the soil. It has been shown in the laboratory that a soil-mix, designed in accordance with the grading and bearing-strength requirements and containing 2% by weight of stabilization oil, possesses in general adequate water resistance. The percentage of the oil is based on the mortar content of the mix. B. M. H. T.

435. Patents on Asphalt and Bitumen. Celotex Corporation. E.P. 531,690, 9.1.41. Appl. 4.7.39. Wear-resisting and resilient surface covering consisting of a number of units of fireboard the interior interstices of which are incompletely filled with bituminous material.

N.V. de Bataafsche Petroleum Maatschappij. E.P. 533,170, 7.2.41. Appl. 2.10.39. Production of unemulsified bituminous substances with improved properties, particularly as regards adhesivity and facility in spreading. The substances are mixed with small quantities of sulphuric-acid esters or arylsulphonic acid esters of lower primary aliphatic alcohols, or with substances from which these esters may be formed.

A. P. Anderson. U.S.P. 2,224,372, 10.12.40. Appl. 18.5.38. Improvement in production of asphaltic hydrocarbons from a straight-run petroleum oil containing substantial amounts of wax and asphaltic hydrocarbons by precipitation with normally gaseous hydrocarbons. By this process the resultant asphaltic hydrocarbons are free from harmful wax.

J. P. Pfeiffer. U.S.P. 2,225,570, 17.12.40. Appl. 2.10.39. Method of improving the adhesive properties of an asphaltic bitumen by combining the bitumen with a small amount of a sulpho-compound.

See also Abstract Nos. 423 and 424. H. B. M.

Special Products.

436.* Containers and Lacquers for Foodstuffs. F. D. Farrow and T. G. Green. *Chem. and Ind.*, 1941, **60**, 95–103.—The article is largely a review of lacquers used in the internal proofing of tins. Under this category is outlined the use of wax for the lining of beverage cans. Owing to the poor adhesion of wax to tin, a special lacquer has first to be applied to the tin. The comparatively low melting point of wax is a disadvantage in dealing with liquids which should be canned while hot. The wax coatings have the advantage of good proofing qualities and no tendency to contaminate flavours.

Brief mention only is made of waxed paper cartons. T. C. G. T.

437. Patents on Special Products. Agricultural and Chemical Products, Ltd. E.P. 530,624, 17.12.40. Appl. 14.6.39. Simultaneous production of higher monohydric alcohols and ethylene from gases containing olefins.

G. G. Luzzatto. E.P. 531,174, 31.12.40. Appl. 27.6.39. Manufacture of a firelighter having a basis of coal, coke, semi-coke, etc., provided with or possessing a proportion of bituminous substance and impregnated, coated, or intimately admixed with an oxygen-carrier.

Standard Oil Development Company. E.P. 531,233, 31.12.40. Appl. 14.7.39. Production of oxy-organic compounds by treating a hydrocarbon or mixture of hydrocarbons having less than 6 carbon atoms per molecule with a gas containing free oxygen at a temperature below the critical temperature of the hydrocarbons, and under sufficient pressure to maintain the hydrocarbons in the liquid phase in the presence of an oxidation catalyst.

N.V. de Bataafsche Petroleum Maatschappij. E.P. 531,359, 2.1.41. Appl. 19.7.39. Process for concentrating highly foaming solutions of capillary-active substances, *e.g.*, aqueous soap solutions, aqueous solutions of alkali or alkaline-earth salts of sulphuric acid esters derived from olefins or alcohols.

Standard Oil Development Company. E.P. 531,383, 2.1.41. Appl. 11.10.39. Continuous process for the reaction of tertiary-saturated hydrocarbons with olefins. An emulsion of a tertiary hydrocarbon in aliquid material capable of catalysing the reaction is mixed with a controlled quantity of a mixture of the tertiary-saturated hydrocarbon and the olefin. The resultant product is then passed through a reaction zone, and part of it removed. An amount of hydrocarbon substantially equal to the volume of olefin–tertiary hydrocarbon mixture is separated out and the remainder recyclized.

General Motors Corp. E.P. 532,630, 28.1.41. Appl. 15.9.39. An improved oil filter comprising a filtering medium having incorporated therein a mixture of *para*-aminophenol, catechol, or *para*phenylenediamine for inhibiting or preventing the formation of resins and acids in the oil.

E. M. Marks and J. W. Johnson. U.S.P. 2,224,158, 10.12.40. Appl. 18.2.36. Method of lubricating Cu–Ag–Cd and Cu–Ni–Pb bearings operated at a high temperature without substantial corrosion. A hydrocarbon lubricating oil incorporating a small quantity of an aryl substituted thiourea is employed.

M. A. Dewey. U.S.P. 2,225,533, 17.12.40. Appl. 26.7.38. Preparation of a transformer oil consisting of a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, and about 0·3% of 2 : 6-*ditert.*-butyl-4-methylphenol and about 0·1% of diphenylamine. The addition agents are effective in combination in retarding the appearance of sludge in the oil.

T. L. Cantrell and J. O. Turner. U.S.P. 2,226,335, 24.12.40. Appl. 14.9.36. Preparation of an oil-soluble organic phosphorus compound suitable as an improvement agent for hydrocarbon oils and effective in imparting extreme pressure characteristics in such oils. The method consists in reacting an olefin and a phenol in the presence of sulphuric acid and treating at least a portion of the resultant product with phosphorus oxychloride to obtain a final product containing 1–5% of phosphorus.

W. H. King and C. Q. Sheely. U.S.P. 2,226,378, 24.12.40. Appl. 26.7.39. Production of partially oxidized products of normally liquid aliphatic hydrocarbons by introducing the hydrocarbons in vapour phase, together with an oxidizing agent, into a reaction chamber at 250–500° C. The amount of hydrocarbon in the hydrocarbon–oxygen ratio is maintained above the explosion limit, and the materials are reacted for not more than 15 sec. in the presence of benzoyl peroxide.

D. L. Wright. U.S.P. 2,228,429, 14.1.41. Appl. 20.9.38. Preparation of a pneumatic percussion-type drill lubricant having adhesive and moisture resistant characteristics. The composition consists of a major proportion of a hydrocarbon lubricating oil, 1–14% of blown rape-seed oil, and 0·1–0·5% of *iso*butylene polymer.

H. B. M.

Detonation and Engines.

438.* Diesel Engines Underground. II. Effect of Adding Exhaust Gas to Intake Air. *Report of U.S. Dept. of the Interior,* Nov. 1940.[1] L. B. Berger, M. A. Elliott, J. C. Holtz, and H. H. Screnk.—The previous report showed that ventilation must be provided to dilute and remove the harmful constituents of the exhaust from diesel engines used in underground working places. The results then reported applied to the operation of engines in normal air, but the possibility of an engine operating in an atmosphere containing its own exhaust gas must be considered. Tests were made on a four-cylinder engine of 70 b.h.p., using a fuel of 50 cetane number; part of the exhaust gas was diverted and mixed with the intake air.

It was found that the concentration of CO in the exhaust was always greater when exhaust gas was present in the intake than when the engine was operated in normal air at the same fuel–air ratio. The increase was most apparent at or near full load; it could not be attributed to CO added to the intake by the exhaust gas. It is suggested that the decrease in oxygen concentration was the fundamental cause.

The concentration of oxides of nitrogen in the exhaust gas decreased as exhaust gas was added to the intake. There was no marked effect on the concentration of aldehydes.

It is concluded that no unreasonable increase in ventilation would be required to maintain a satisfactory working environment if the CO_2 in the atmosphere were not greater than 1%; the underground atmosphere should be analysed frequently to ensure satisfying conditions. Diesel engines should be prohibited where the ventilation is locally inadequate, and " short-circuiting " of the exhaust between the exhaust outlet and air intake of the engine should be avoided. K. A.

439.* Engine Bearing Temperatures (Third Report—Bench Tests). Report of the Automobile Research Committee, prepared by J. Spiers. *Instn. Aut. Engrs. J.*, February 1941, **9** (5), 7–39.—This report deals mainly with the effects of diametral clearance on bearing temperatures at rubbing speeds up to 2350 ft./min. Details of the engine and bearings used are given in Abstract No. 427. Bearing temperatures were measured by means of thermocouples connected to slip-rings on the crankshaft. With clearances of the order of 0·0005 in. oil inlet temperature had little, if any, effect on the bearing temperature, and at high speeds such a bearing would tend to seize. With clearances up to about 0·0015 in. oil cooling as a means of reducing bearing temperatures appears to be of little value. With clearances above 0·0035 in., although 60% or more of any oil inlet temperature reduction is passed on, the actual bearing temperatures are scarcely high enough to justify oil cooling on this account in an engine of the size tested.

The influence of oil pressure on bearing temperature was small, as was also the effect of water-jacket temperature. It is considered that efficient ventilation of the crankcase interior by cool air might have a beneficial effect on big-end temperatures. Motoring tests showed that bearing temperatures were almost independent of load. The addition of 1% methyl-dichlorstearate to the oil produced no measurable differences in temperature throughout the speed range, as compared with the untreated oil; it is inferred that heat generation in the bearings is entirely due to viscous friction, *i.e.*, lubrication is of the fully fluid type.

The tests confirmed that the main factors determining engine bearing temperatures are diametral clearance, oil viscosity, and speed. In this respect the use of light oils of high viscosity index is advocated. Bearing temperatures rise linearly with speed, and increasing speed tends to raise main bearing temperatures more than big-end temperatures. K. A.

440. Patents on Detonation and Engines. I. G. Farbenindustrie A.-G. E.P. 532,424, 23.1.41. Appl. 30.8.39. Production of non-knocking motor fuels by catalytically cracking hydrocarbons obtained from carbon monoxide by reaction with hydrogen, mixed with a paraffinic-base petroleum oil or fractions thereof.

H. Kaufmann. U.S.P. 2,228,118, 7.1.41. Appl. 3.5.39. Production of a non-knocking motor fuel by heating to cracking temperature a mixture of a normally

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[1] See also Abstract No. 1427, Oct. 1940.

non-gaseous reduction product of carbon monoxide with a normally non-gaseous hydrocarbon product, in the presence of a stationarily arranged catalyst having a splitting action and of a non-oxidizing gas under a pressure above 350 atmospheres.
H. B. M.

Coal and Shale.

441.* Technical Study of Transvaal Torbanite. S. L. Neppe. *J. Inst. Petrol.*, 1941, **27** (208), 31–65.—Torbanite consists of mineral matter which is essentially inherent with the organic constituents which make up the volatile and fixed carbon. The different grades of Transvaal torbanite may be considered as having a common origin in one parent substance of high fuel ratio. There is little difference between the ultimate products of deterioration of torbanite, irrespective of the quality of the original minerals. It is probable that during the stages of deterioration depolymerization processes play a big part in the chemistry of the kerogen molecules, such deterioration offering some striking parallelisms to certain cracking reactions. In both processes hydrogen is mainly removed as a result of which the carbon contents of the volatiles show a steady increase up to a limit. Beyond this point in both cases carbon is separated. This theory of the deterioration of torbanite is substantiated by additional interesting facts observed and recorded by the author. B. M. H. T.

Economics and Statistics.

442.* Opportunities in the Petroleum Industry. Anon. *Chem. Met. Eng.*, June 1940, **47** (6), 416–422.—The paper is in two parts: the first deals with the petroleum industry as a whole and its structure; the second with the opportunities afforded to the chemical engineer in the industry. The treatment is of the American petroleum industry. A. H. N.

BOOK REVIEW.

U.O.P. Laboratory Test Methods for Petroleum and its Products. Published by the Universal Oil Products Incorporated, 310 South Michigan Avenue, Chicago. 1940. Price $3.

The first edition of this book was issued in 1937, and was intended particularly for use by the refiner with limited personnel and literature facilities to supplement the A.S.T.M. methods of test. The revised edition is issued in loose-leaf form of binding, and index tabs are provided for the various sections, and it is stated that as revised methods become available they will be distributed without charge to holders of the book.

A number of the methods given in the earlier edition have been eliminated, and there has been a thorough revision of the methods which have been retained; the methods given have been either developed by the U.O.P. laboratories, or tested out by them.

The following will illustrate some of the types of analytical procedures covered:

> Salt content of charging stocks; carbon and hydrogen analysis, by a semi-microscopic method; volumetric determination of sulphur; molecular weight of petroleum; nitrogen in petroleum; laboratory preparation of asphalts; routine high vacuum distillation of heavy oils; analysis of gasolines for paraffin, olefine, naphthenic and aromatic content.

A large section of the book deals with the analysis of gases, including the determination of gaseous olefines by catalytic hydrogenation and the fractional distillation of C_4 and C_5 hydrocarbons.

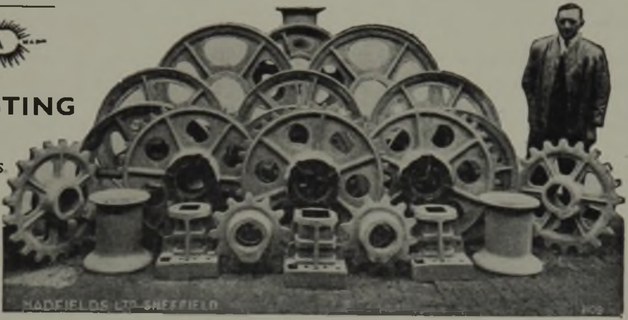
Under fuel oils a method is given for the determination of Redwood Admiralty viscosity at 32° F., and this does not appear to be in accord in all details with the standard Admiralty procedure.

The method for the hydrocarbon analysis of gasolines is based on the determination of the percentage of olefines from the bromine number and the molecular weight, and the aromatic hydrocarbons by specific dispersion, and the naphthene/paraffin ratio from the refractive index and by calculation. Naturally in a book of this kind no evidence is given of the accuracy of the methods employed or of the justification for using refractive index and specific dispersion methods in preference to the much simpler aniline-point method.

An index is provided, which is very complete.

By reason of the fact that it collects together the methods of analysis which have been tried out and which are not included in the standard methods of testing, U.O.P. Laboratory Test Methods will be found to be of considerable value to all laboratories engaged in the testing of petroleum products.

F. H. GARNER.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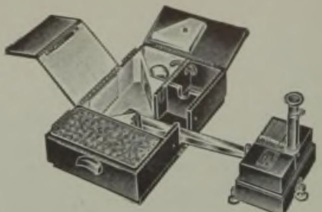

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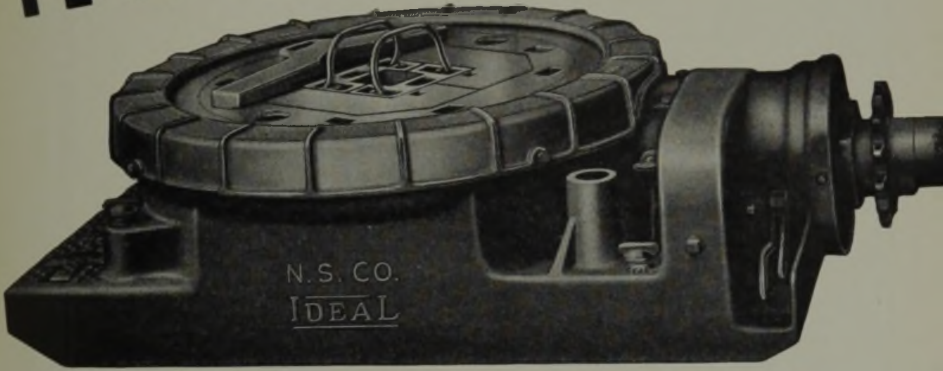
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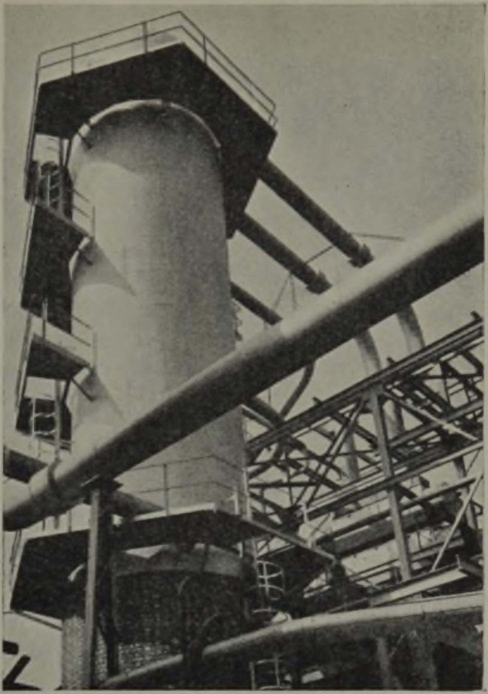

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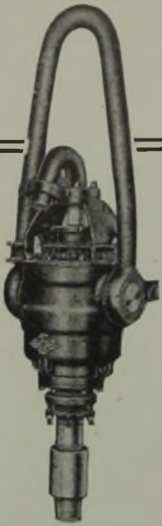

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