

THE CYCLIZATION OF HYDROCARBON MIXTURES.*

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INTRODUCTION.

THE conversion of non-aromatic hydrocarbons into aromatics within convenient temperature range constitutes one of the most important advances in recent hydrocarbon chemistry. The process is attractive not only for the production of high-octane fuel, but also for the production of pure aromatic hydrocarbons and for many potential uses in analytical chemistry, etc.

Considerable work has been done on the dehydrogenation-cyclization reactions of pure hydrocarbons, but little has been published on the conversion of hydrocarbon mixtures in this way. In the present work, a preliminary examination of the possibilities, there is no contribution to the theory of the mechanisms of cyclization reactions, but some interesting facts are disclosed and some potentialities of the dehydrogenation cyclization process are indicated.

By "thermal" and "catalytic" aromatization two different processes are understood. In the first the nature of the aromatic hydrocarbons produced depends on the temperature, and in the second, on the catalyst and the feed. The thermal aromatization of heptane, for example, would lead to an equilibrium mixture (theoretically) of benzene and other aromatics, while the cyclization of the same hydrocarbon would produce toluene.

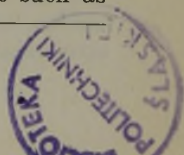
PREVIOUS WORK.

When the catalytic aromatization of hydrocarbon mixtures is considered, reactions other than pure dehydrogenation-cyclization must be expected to influence the conversion. For this reason aromatization in general is considered in the literature review below. There is considerable published work on the production of aromatics from other hydrocarbons, and only a selection is indicated here.

Aromatics from Unsaturateds.

In 1931, Mailhe and Renaudie¹ heated mixed amylenes up to 670° C. for several hours, and obtained aromatics in the product, together with some tar. Taylor and Turkevich² converted various branched and straight-chain olefines into mixtures containing aromatics using chromium sesquioxide gel at temperatures ranging from 400° to 475° C. Various olefines and paraffins were converted into aromatics by Grosse, Morrell, and Mattox³: octane was converted into a mixture containing aromatics at temperatures of 450–700° and contact times of 0.1–10 seconds over catalysts such as

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Cr, Mo, V, Ti, on activated alumina. Cyclic olefines have been converted into aromatics by various workers,^{4, 5, 6} and some simple cyclic diolefines were similarly converted,^{7, 8, 9} using Pd catalyst in both cases. Using Cr_2O_3 gel, Goldwasser and Taylor¹⁰ investigated the aromatization of heptane, heptene, and hexene isomers.

The process of cyclization involves dehydrogenation, and a useful summary of the literature on catalytic dehydrogenation of hydrocarbons is given in the *Twelfth Report of the Committee on Catalysis* (New York, 1940).

Paraffins to Aromatics.

Egloff¹¹ reported as early as 1916 the conversion of hexane into toluene and other aromatics using a steel tube at temperatures from 450° C. to 725° C. More recently the U.O.P. workers^{3, 12} have converted hexane and heptane into aromatics and unsaturateds over oxides of Cr, Mo, Ti on alumina and over Cr_2O_3 gel, the products in many cases containing more than 50 per cent. aromatics. Moldavski and co-workers¹³ converted octane and heptane into aromatics using Cr_2O_3 gel and also zinc oxide.

In their rather comprehensive work these workers showed that *n*-octane passed over Cr_2O_3 gel at 400° C. produced mainly *o*-xylene and ethyl benzene together with some *m*- and *p*-xylene. Diisobutyl was converted into *p*-xylene, and butyl benzene converted into naphthalene under similar conditions. Conversion losses were found of the order of 50 per cent., but volumes of the order of only 20 c.c. were used. Their general conclusions were that increase in the contact time increases aromatics and decreases unsaturated hydrocarbons in the products from paraffins, while naphthenes produced are negligible. Other catalysts used for the conversion of octane included TiO_2 , MoO_2 on charcoal, MoS_2 , carbon on iron turnings¹⁴ and nickel on zinc oxide.¹⁵ For the aromatization of the decanes chromium-copper-phosphorus and chromium-molybdenum¹⁶ have been used. In order to avoid carbon formation, which is likely to accompany dehydrogenation at the higher reaction temperatures when using nickel catalysts, it has been suggested in a recent patent¹⁷ that the reaction should be carried out in the presence of steam in a chromium-steel tube.

Taylor and Jovis found that Cu-Mg catalysts are less active than Ni for carbon-carbon bond splitting in dehydrogenation-cyclization reactions.

Naphthenes to Aromatics.

*cyclo*Hexane has been converted into benzene over various catalysts at temperatures varying from 190° C. to 540° C. Moldavski and co-workers¹⁴ used ZnO , TiO_2 , MoO_2 on charcoal, MoS_2 , active charcoal, and carbon on iron; Balandin¹⁸ used Ni on alumina and later¹⁹ alumina alone. Zelinsky²⁰ used palladium at 300° C. to obtain benzene as early as 1911, but recently he prepared toluene from *cyclo*hexane using Ni on $\text{Al}(\text{OH})_3$, and benzene when using platinum.²¹ In 1936, Ipatieff and Komarewsky²² produced toluene, benzene, and methane from *cyclo*hexane by passing it over nickel-aluminum at 350° C. Alumina,²³ copper,²⁴ and copper-chromium²⁵ have also been used successfully. Jubhard²⁶ showed that Fe, Cu, Cd and Pb oxides when mixed with a nickel catalyst reduced its activity for this conversion, while Zn, Mn, Cr, Ce, Th, Al and Be oxides increased it. Toluene

has been identified as a product from methyl *cyclohexane* using Al_2O_3 ¹⁹ and Cu,²⁴ from dimethyl *cyclohexane* using Cu,²⁴ from ethyl *cyclohexane* using Ni-Al²² and from *cycloheptane* using Pt on charcoal. While five-membered carbon rings offer great resistance to dehydrogenation, rings of more than six carbon atoms often undergo ring contraction under similar conditions.

Hydrocarbon Mixtures.

Dehydrogenation and cyclization have been recognized by various workers as important processes for the production of improved motor fuels. Karzhev and others¹⁶ have aromatized Grozny aviation petrol with various catalysts such as copper chromite, chromium, chromium-molybdenum and nickel, products containing 80 per cent. aromatics being obtained in some cases.

Uranium, titanium and thallium oxides have been used as catalysts in the aromatization of kerosene.²⁷ More recently Koch²⁸ aromatized a fraction of synthetic gasoline with vanadium oxide and chromium oxide supported on alumina.

Mechanism of the Reactions involved in Dehydrogenation-cyclization.

The mechanism of dehydrogenation-cyclization is still a hypothetical matter, but some of the facts found by workers studying the fundamentals of the reactions may illuminate certain technical aspects of the conversion of non-aromatic into aromatic hydrocarbons.

Pitkethly and Steiner,²⁹ considering the dehydrogenation-cyclization of heptane, give evidence supporting their suggestion that heptene is an intermediate product of the reaction only in the sense that it is in equilibrium with the half-hydrogenated state. They showed that the paraffin-olefine equilibrium is not established under the conditions of their experiments, which were carried out at 475° C. over a dehydrogenation catalyst and with a contact time of 20 ± 4 seconds.

Hoog, Verheus, and Zuiderweg³⁰ examined a number of hydrocarbons passed over Cr_2O_3 gel at 465° C., and concluded that where the hydrocarbon structure permits of direct formation of a six-membered ring, such structures are aromatized to a large extent, but other structures are not appreciably aromatized. In the aromatization of hydrocarbon mixtures, therefore, the percentage aromatics produced by dehydrogenation-cyclization will depend on the proportion of paraffin hydrocarbons with suitable structures.

Taylor and Turkevitch² studied the conversion of various olefines, including 2-methyl-pentene-2, 2-ethyl-butene-1, heptene-1, heptene-3, 5-methyl-hexene-2 and octene-1, and concluded that the rate of conversion of olefinic hydrocarbons into aromatics is initially more rapid than that for saturated hydrocarbons, but that the deterioration in the activity of the catalyst is also more rapid. They suggested that this latter fact is due to the number of side reactions involved and deposition of carbonaceous material on the catalyst surface.

The Catalysts Used.

The various catalysts which have been used for the production of aromatics from unsaturateds, paraffins and naphthenes are the metals of

Group VIII (Co, Ni, Pt, and Pd), the transition metals of Groups V and VI (V, Nb, Ta, Cr, Mo, W, and U) and the oxides of the transition metals of Groups IV, V, and VI (Ti, Zr, Ce, Th, V, Nb, Ta, Cr, Mo, W, and U), either singly or in combination. Non-metals such as silica gel and activated carbon have also been shown to be active for this conversion. Various carriers have been used, and it has been suggested that carriers of any inert material are efficient if they have a large surface area. Florida earth and similar materials, after treatment with water, dilute caustic soda, ammonia, etc., are suggested for use as carriers³¹ for catalysts used in the dehydrogenation of unsaturated hydrocarbons. Activated granulated alumina, however, seems to be recommended by later American workers.

The processes of ring closure of C_6 - C_{12} paraffins and olefines, of course, involve dehydrogenation. In the reactions studied for pure hydrocarbons the process has been one purely of dehydrogenation-cyclization, involving essentially no scission of a C-C bond, although some decomposition usually occurred. Since it had been shown that Ni, Co and Fe were catalysts which activated the C-C bond, Taylor and Turkevich² suggested that these metals are of doubtful utility for maximum dehydrogenation-cyclization, and copper was rejected because of the sintering observed at about 400° C. It is worth mentioning here, however, that Adkin's catalyst, copper chromite, does not sinter readily at this temperature, and that copper chromite catalysts appear to be active in the aromatization of hydrocarbon mixtures.¹⁶ On the basis of his own fundamental work on activated adsorption, where it had been shown that oxide hydrogenation-dehydrogenation catalysts exercise their activity at higher temperatures than the corresponding metal catalysts, and considering the thermodynamical requirements for the cyclization reaction, Taylor investigated oxide catalysts. Turkevich and Taylor³² and Howard and Taylor³³ showed that the position of chromium sesquioxide gel for hydrogenation-dehydrogenation reactions, claimed by Lazier and Vaughan³⁴ to be unique, is only one of degree. They indicated that the activated adsorption of hydrocarbons on oxide catalysts is negligible below 300° C., but at higher temperatures there is definite evidence of interaction between the gases and the surface. In accordance with their general theory, these workers considered the conversion of paraffinic into aromatic hydrocarbons to involve four steps:—

- (1) Activated adsorption of the paraffin on to the surface.
- (2) Surface dehydrogenation with the formation of adsorbed aromatic and adsorbed hydrogen.
- (3) Desorption of hydrogen.
- (4) Desorption of aromatic.

The rate of conversion of paraffin into aromatic would be that of the slowest of these steps. It was concluded that chromium sesquioxide, principally, and other oxide catalysts are ideal for cyclization, and that although there is no data on the relative adsorption of aromatics and paraffins on the catalyst surface, it was assumed that the paraffins can compete effectively for the surface with the aromatics.

More recently, Taylor and Fehrer⁴⁵ have found that Cr_2O_3 and to a smaller extent Mo, Mn, Ce, and V catalysts are poisoned for aromatization

by olefines. Two-component gel catalysts of Cr_2O_3 with Cu, Ni, Pd, MnO, ZnO, MoO_2 , SiO_2 , ZrO_2 , and SnO_2 were studied for the dehydrogenation-cyclization of *n*-heptane. The ZrO_2 and SnO_2 catalysts were superior to Cr_2O_3 alone.

Moldavski, Kamusher, and Kobyl'skaya¹⁴ have reported that glass and silica gel are inactive, whilst ZnO, TiO_2 , MoO_3 , and MoS_2 are active in the aromatization of *n*-octane, and have pointed out that catalytic cracking of the higher hydrocarbons can yield either complex aromatics which lose side-chains or fragments which join together to form aromatics.

Efficient dehydrogenation-cyclization catalysts containing in order of efficacy, oxides, of the metals of Groups VI, V, and IV, have been developed by Grosse, Morrell, and Mattox,¹² minor proportions of the metals being deposited on various carriers by impregnating the carrier with a solution of a decomposable compound of the metal. Their results show that at all contact times a vanadium-molybdenum catalyst is less active than a simple chromium catalyst, but that the chromium-molybdenum and chromium-vanadium catalysts give better results at longer contact times than any of the single metal catalysts. The triple chromium-vanadium-molybdenum catalyst is found to be even more active than the double catalysts. If equal atomic proportions of the promoting metals were used in each case—and this appears to be the most reasonable way of comparing the activity of the various metals—then their results differ from those expected from a consideration of the hypothesis due to Griffith,³⁵ who postulated that "the optimum promoter concentration is a function of the catalyst and not of the promoter."

Work in connection with the Fischer-Tropsch process indicated that cobalt and allied metals are susceptible to poisoning by sulphur, but copper chromite catalyst has been stabilized against sulphur for hydrogenation catalysts by the incorporation of barium. Molybdenum trisulphide has been claimed as a desulphurization-hydrogenation catalyst, and sulphur itself, of course, is a dehydrogenating agent.

Taylor and Turkevich² found that water vapour was strongly adsorbed on chromium sesquioxide gel and was a marked poison for the cyclization reaction, but no difference in activity could be detected for heptane left in contact with water and heptane which had been dried using phosphorus pentoxide. Water appears to be a reversible poison, whereas ethylene was found to poison the catalyst irreversibly.

Much of the published work is very useful, but care must be taken in its interpretation, as different apparatus and different analytical methods used make comparative study difficult. In the present work, a small part of the published work was repeated, in order to achieve some arbitrary standard conditions necessary for a comparative chemical approach.

THERMODYNAMIC CONSIDERATIONS.

As early as 1931 Frohlich observed,³⁶ that thermodynamic considerations led to the conclusion that all the hydrocarbons are interrelated in such a manner that it should be possible to pass from one to another almost at will.

Thermodynamic considerations indicate the temperature and pressure at which a given reaction can occur to a useful extent, but can, however, be only a general guide as care must be taken in the interpretation of thermo-

dynamic data because the values of free energy of formation, especially at the higher temperatures, are known accurately for only a very few hydrocarbons.

In 1937 Thomas, Egloff, and Morrell³⁷ collected most of the work that had been done on the thermodynamic properties of hydrocarbons and discussed the differences between results obtained from calorimetric measurements and those calculated from Raman and infra-red spectra. New free-energy equations were derived for straight-chain paraffins and olefines with a terminal double bond, and using these, approximate free-energy values were calculated for hydrocarbons where other data were non-existent. With the free-energy values for relevant hydrocarbons at 298° K. and 1000° K. thus collected, various reactions involved in cyclization have been considered. Thermodynamics, however, can give no indication of the rate of a reaction, and as this is often the most important factor, the course of a reaction is not indicated. But such study gives information on the temperature range in which to look for a catalyst.

The method used in the following calculations is based on the accepted relation :

$$\Delta F_T^\circ = -RT \log_e K \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$K = e^{-\frac{\Delta F_T^\circ}{RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Where

$$\begin{aligned} \Delta F_T^\circ &= \text{free energy change,} \\ K &= \text{equilibrium constant,} \\ T &= \text{absolute temperature.} \end{aligned}$$

It is obvious that if $\Delta F_T^\circ = 0$, $K = 1$, if ΔF_T° is +ve, K is less than 1, and if ΔF_T° is -ve, K is greater than 1.

When K is greater than 1, the reaction can be said to proceed to a convenient extent—i.e., it is “permissible.”

An approximate linear relationship, within the limits of accuracy of the free-energy data :—

$$\Delta F_T^\circ = A + BT \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is assumed for the reactions considered; A and B are then calculated using the values of ΔF_T° at 298° K. and 1000° K. for standard free energies of formation from graphite and hydrogen at atmospheric pressure for the individual components of a reaction. Equation (3) is then solved, and the temperature to give a zero value for ΔF_T° —the neutral equilibrium temperature—thus calculated.

The main assumption in the calculation is, then, that the deviations of the free-energy temperature relationships from linear are within the errors involved in the determination of the free energy values. Ewell³⁸ showed the significance of the neutral equilibrium temperature, and pointed out that the free energy temperature relationship is linear if the specific heat change with temperature is small. Consider the fundamental equation for a reaction at T° K :

$$\Delta F_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Where

$$\begin{aligned} \Delta F_T^\circ &= \text{free energy change,} \\ \Delta H_T^\circ &= \text{heat content change,} \\ \Delta S_T^\circ &= \text{entropy change and} \\ T^\circ &= \text{absolute temperature.} \end{aligned}$$

If at $T^\circ \text{K}$. equation (4) represents a reaction, the free energy change involved at $T_1^\circ \text{K}$ is given by equation (5) :—

$$\Delta F_{T_1}^\circ = \left[\Delta H_T^\circ + \int_T^{T_1} \Delta C_p^\circ dT \right] - T_1 \left[\Delta S_T^\circ + \int_T^{T_1} \frac{\Delta C_p^\circ \cdot dT}{T_1} \right] \quad (5)$$

Where ΔC_p° = change in specific heat (at constant pressure of 1 atmosphere). Since this factor ΔC_p° would be small in the cyclization reaction, the assumption of a linear relationship between ΔF_T° and temperature is justified, for if ΔC_p° is neglected, equation (5) becomes :

$$\Delta F_{T_1}^\circ = \Delta H_T^\circ - T_1 \Delta S_T^\circ \quad . \quad . \quad . \quad (6)$$

Using equations (2) and (3) and the data collected by Thomas, Egloff, and Morrell,³⁷ many interesting calculations of the neutral equilibrium temperature for various reactions at atmospheric pressure have been made, some of which are given in Table I below, together with the constants A and B in the equation $\Delta F_T^\circ = A + BT$. The accuracy of the calculations depends in each case on the factor C_p and on the free-energy values.

TABLE I.

Reaction.	Neutral equil. Temp., °C.	A.	B.	Conclusions.
1 <i>n</i> -Heptane to toluene, $\text{C}_7\text{H}_{16} \rightarrow \text{C}_7\text{H}_8 + 4\text{H}_2$	283	60,700	-109	Reaction "permissible" above 283° C.
2 <i>n</i> -Heptane to <i>n</i> -heptene-1, $\text{C}_7\text{H}_{16} \rightarrow \text{C}_7\text{H}_{14} + \text{H}_2$	610	30,900	- 35	Reaction "permissible" above 610° C.
3 Toluene to naphthalene and isobutene, $2\text{C}_7\text{H}_8 \rightarrow \text{C}_{10}\text{H}_8 + \text{C}_4\text{H}_8$	—	20	+6.04	Reaction is not "permissible."
4 Toluene to naphthalene and elements, $2\text{C}_7\text{H}_8 \rightarrow \text{C}_{10}\text{H}_8 + 4\text{C} + 4\text{H}_2$	1,355	142,300	+ 87.4	Reaction "permissible" at very high temperature.
5 <i>n</i> -Heptane to naphthalene and elements, $2\text{C}_7\text{H}_{16} \rightarrow \text{C}_{10}\text{H}_8 + 4\text{C} + 12\text{H}_2$	199	135,500	-287	Reaction "permissible" above 199° C.
6 <i>n</i> -Heptene-1 to toluene, $\text{C}_7\text{H}_{14} \rightarrow \text{C}_7\text{H}_8 + 3\text{H}_2$	129	29,760	- 73.8	Reaction "permissible" above 129° C.
7 Toluene to benzene and elements, $\text{C}_7\text{H}_8 \rightarrow \text{C}_6\text{H}_6 + \text{C} + \text{H}_2$	115	9,300	-239	Reaction "permissible" above 115° C.
8 cycloHexane to benzene and hydrogen, $\text{C}_6\text{H}_{12} \rightarrow \text{C}_6\text{H}_6 + 3\text{H}_2$	253	49,800	-947	Reaction "permissible" above 253° C.

No calculations of the actual equilibrium constants at various temperatures are given above, but these are, of course, important when considering specific reactions. The reactions with the formation of naphthalene are interesting, *n*-heptane being unstable to this compound under the conditions of cyclization reactions. In the present work naphthalene formation was found to be quite general.

Results similar to those above were obtained by Taylor and Turkevich,² who considered the simpler possibilities of the decomposition of hexane to form :—

- (1) Paraffins and olefines.
- (2) Higher paraffins and hydrogen.
- (3) Higher and lower paraffins.
- (4) Carbon and hydrogen.
- (5) Olefine and hydrogen.
- (6) *cyclo*Paraffin and hydrogen.
- (7) *cyclo*Olefine and hydrogen.
- (8) Aromatics (benzene) and hydrogen.

These workers came to the following conclusions : Two paraffins cannot form a higher paraffin by the elimination of a molecule of hydrogen.

In the cyclization of hexane to benzene the equilibrium is completely on the side of benzene at 327° C.

Dehydrogenation of hexane to olefine and *cyclo*hexane does not become appreciable below 527° C., but such dehydrogenation, even above this temperature, is not a serious competitor to the cyclization to benzene, since the olefinic product is unstable with respect to aromatics above 277° C.

Cracking to olefines and lower paraffins, decomposition to elements, and disproportionation are all serious competitors to cyclization. Generally, it may be concluded that the possibility of conversions of straight-chain paraffins, branched-chain paraffins, olefines, and naphthenes to aromatics expected on the basis of the low energy resonance structure of the benzene ring is indicated in many cases by thermodynamic calculations, but other reactions involving the splitting of C—C bonds are serious competitors. To prevent undesirable reactions it seems, therefore, that for the aromatization of single compounds a catalyst which activates the C—H bond only should be used.

CYCLIZATION OF HYDROCARBON MIXTURES.

In preliminary runs a chromium sesquioxide catalyst prepared from chromic acid deposited on Floridin was found to have little effect, while a similar catalyst prepared from chromium nitrate was much more active for cyclization. The activity of these catalysts, however, was considerably increased by using activated alumina as the carrier.

EXPERIMENTAL METHOD.

The apparatus used consisted essentially of a constant rate of delivery burette, a catalyst tube, a receiver, and a gas meter. The feed was introduced through a mercury seal, the catalyst tube heated in an electric furnace, and the receiver cooled in ice-salt. To observe the temperature of the electric furnace a pyrometer accurate to $\pm 5^\circ$ C. at 350° C. was used. The catalyst was held in position in the tube by glass wool and broken glass. In order to avoid unnecessary cooling of the catalyst and because of the endothermic nature of the reactions, a preheater was introduced, and this vaporized the liquid feed at about 400° C. To facilitate the introduction of

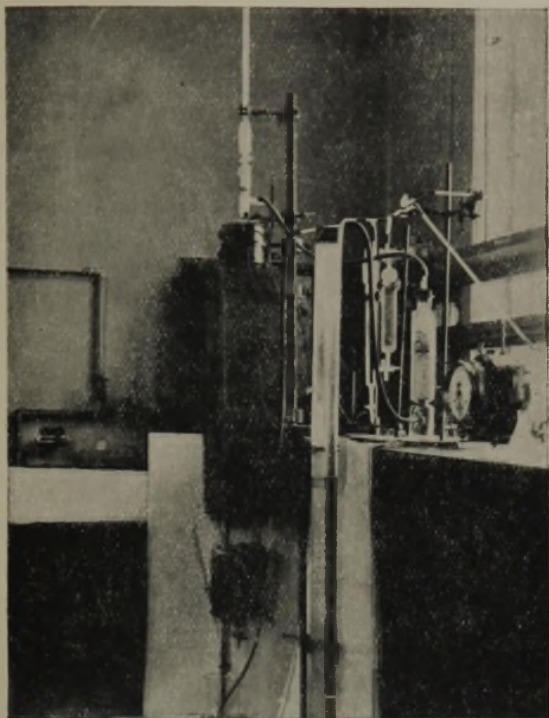


FIG. 1.

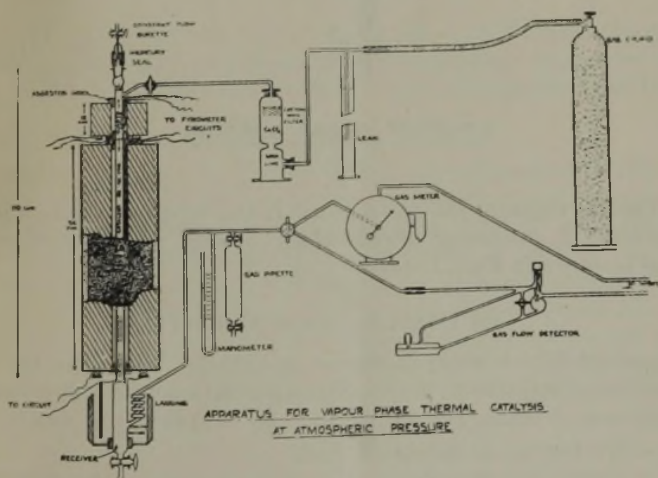
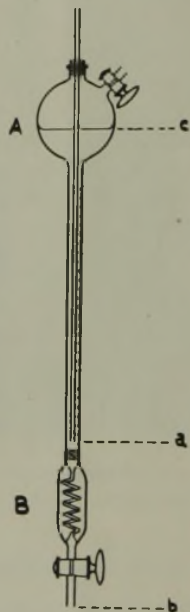


FIG. 2.

gases into the catalyst tube the end of the tube was fitted with a ground-glass joint and interchangeable stoppers.

Although there was a slight directional slope on the catalyst tube, the liquid charge remained in contact with the broken glass in the preheater long enough in some cases partly to decompose and deposit tar.

Later the apparatus was modified and the catalyst tube placed in the vertical position, in order to decrease liquid contact time in the preheater and to facilitate continual removal of the product with the receiver at the lower end of the catalyst tube; for the connection of catalyst tube and receiver it was found advisable to use a mercury seal. A manometer was fitted and a sensitive flowmeter used as a gas detector. This flowmeter



CONSTANT FLOW BURETTE

FIG. 3.

was not used to measure the gas produced, and by-passes were introduced for connecting a gas-meter or absorbing bottles when necessary. The apparatus is shown in Figs. 1 and 2.

THE CONSTANT-FLOW BURETTE.

The constant-flow burette is shown in Fig. 3. When the tap in *A* is closed and liquid is run from the burette, a partial vacuum is developed in *A*. The pressure in *A* being, (Atmospheric — $ac \times \rho$) inches of water.

where *c* = level of liquid in burette bulb,

a = level of liquid in tube—i.e., at the bottom of the inner tube for constant flow,

ρ = density of liquid.

The driving head is then *ab*, and there is a constant resistance to flow at *B*. Hence, since *a* is at atmospheric pressure, the flow will be constant for any setting of *a*, if pressure at *b* is constant.

Three notable disadvantages of this burette in the present work are : first, the necessity for a filter to prevent interference with the capillary ; second, the rate of flow depends on the pressure at *b* and hence varies with the gas formed in the catalyst tube, and third, the rate of flow depends on the density of the charge. Again, the rate of flow cannot be measured while a run is actually in progress.

Attempts were made to eliminate errors due to back pressure by connecting the upper part of the catalyst tube with the sliding tube of the burette, and thus making the pressure at *a* and *b* equal in all circumstances. These attempts failed because of condensation of vapours in the connecting tube.

It was found, however, that although the back-pressures were different for different reactions, that during short runs the back pressure was nearly constant, and consequently the rate of flow was constant. The actual rate was then found from the total liquid passed and the duration of the run. It was not possible, then, to use exactly the same rate of charge for all experiments, but conditions were approximately the same in most cases.

The Standard Conditions.

For a comparative study of the reactions of various hydrocarbons and mixtures some standard conditions were required. It was not required that these conditions should be the best possible obtainable for any particular aromatization reaction, but that the conversion should proceed to a reasonable extent. The arbitrary conditions chosen were therefore not the best possible conditions for the aromatization of any particular hydrocarbon. By controlling conditions as near to "Standard" as possible, experiments made using different apparatus were made comparable.

The liquid space velocity was 0.33 c.c. of liquid per c.c. of catalyst per hour.

The liquid products were cooled at -5° to -14° C., and vapours which passed through a condensing spiral at this temperature range were measured as gas. The preheater temperature was controlled at $250-300^{\circ}$ C.

Preparation of the Molybdenum Catalyst.

20 grams of A.R. ammonium molybdate were dissolved in 100 grams of 0.800 A.R. ammonium hydroxide and an equal volume of water. This solution was poured slowly on 250 grams of Grade A activated alumina 8-14 mesh (Alorco) which had been heated at 350° C. for 3 hours and cooled in a vacuum desiccator without desiccant. The mass was stirred for about 30 minutes when the solution was completely and uniformly absorbed by the alumina. This was dried at 100° C. for 1 hour and then left overnight at 310° C. $\pm 10^{\circ}$ C. The catalyst was introduced into the reactor and reduced by passing a stream of dry hydrogen for 3 hours at 350° C., and then remaining hydrogen was swept away with nitrogen. It was shown that for short runs the temperature of reduction of the catalyst did not effect the cyclization reaction of *n*-heptane. The unpromoted catalyst thus prepared contained 2 per cent. molybdenum, and was in a very convenient and stable form.

The catalyst was regenerated by sweeping out any hydrocarbons with nitrogen, switching off the furnace, and then passing dry air with the preheater at 550° C. until the carbonaceous deposits on the catalyst had been reduced. Remaining air was then swept out with nitrogen, and hydrogen passed for 3 hours to effect reactivation by reducing the molybdenum oxides.

ANALYTICAL METHOD.

A 25 theoretical plate packed column and laboratory distillation unit for distillation of volumes of the order of 500 c.c. was constructed for preliminary distillations.

Chemical Analysis for Aromatics.

When only approximate indication of composition was required, the aromatics were estimated by aniline-point determinations before and after absorption with 98 per cent. sulphuric acid, following the removal of the unsaturateds by absorption in 80 per cent. sulphuric acid. Nitration methods appear preferable, however, where more accurate knowledge is required and, because of the small volumes available from fractional distillation, the method of Manning and Shepherd³⁹ was examined. Their method consists in passing a stream of air over the hydrocarbons and absorbing the aromatic and unsaturated vapours in a nitrating mixture. The weight of the aromatics and unsaturateds is thus obtained and the percentage paraffinic material found by difference. The nitrating solution is heated to 100° C. to complete the nitration, during which treatment the unsaturateds are oxidized to form products soluble in water or caustic soda solution. The nitrated aromatics are extracted with benzene, which is removed by distillation, and the weight of the original aromatics is estimated from the weight of the nitro-compounds. These workers found the method gave results correct to within ± 0.1 per cent. for mixtures containing 4.4, 18.4, 48.5 per cent. benzene.

In the present work, for the mixtures containing 10–60 per cent. benzene or toluene and a maximum of 30 per cent. unsaturateds the method was found to be accurate to ± 1 per cent. The estimation of aromatics was not high if the nitro-compounds were dried for a few hours in a vacuum desiccator. For high-percentage unsaturateds accurate results could not be obtained even when an additional absorber containing 70 per cent. sulphuric acid was introduced as recommended by Manning and Shepherd. A comparison of the results obtained by extraction of the nitro-compounds after pouring the nitrating mixture into ice-cold water with those obtained by separating directly after the same treatment and cooling for several hours through a tared sintered-glass Gooch crucible, showed differences of the order of 1 per cent. on the whole mixture for the estimation of benzene and toluene. The second method of separation of the nitro-compounds also gave pure crystalline products (dinitrobenzene and trinitrotoluene), which were easily dried, and in many cases their purity was not measurably improved by recrystallization. When the nitro-compounds were extracted, however, the products were usually less pure, and their melting points were increased on recrystallization. The Manning–Shepherd absorption train was proved quite successful for the hydrocarbon mixtures similar to benzole,

and finally the modified absorber due to Gooderham⁴⁰ was introduced. The method selected was, in general, that of distillation and fractionation followed by estimation of aromatics, unsaturateds and paraffinics by the absorption-train method supplemented by examination of the nitrated aromatic compounds and further examination when necessary. Naphthenes were generally negligible throughout.

Estimation of the Unsaturateds.

The most usual method for the estimation of unsaturateds is by bromine absorption with estimation of the molecular weight from the distillation range on the assumption that only aliphatic mono-olefines are present. Hoog, Verheus, and Zuiderveg³⁰ used this method in similar catalytic cyclization work, followed by removal of the unsaturateds with thioglycollic acid in a homogeneous propionic acid solution at room temperature prior to the estimation of the aromatics by absorption in 98 per cent. sulphuric acid. Treatment with thioglycollic acid can be used for the estimation and isolation of the unsaturateds, but the cost of the reagent in this country is prohibitive.

The determination of bromine numbers for hydrocarbon mixtures was studied in some detail.⁴¹ The evidence obtained suggested that bromine absorption cannot be used to estimate the actual percentage unsaturateds present in complex mixtures, although, using the titration technique of Lewis and Bradstreet,⁴² it is possible to find quickly a value for comparative purposes. For the normal mixtures met with in this work the absorption train gives satisfactory results for the estimation of unsaturateds, although it gives no indication of their qualitative composition. The method selected for unsaturateds was therefore absorption train analyses supplemented when necessary by bromine-number determinations.

Estimation of Paraffins and Naphthenes.

Paraffins and naphthenes were estimated together in the absorption train, but the production of naphthenes has not been observed during cyclization reactions, and generally analysis for naphthenes was not made, although by the introduction of a cooled trap in the absorption train it was found possible to collect small samples of paraffinic constituents for further examination.

Determination of Sulphur.

The hydrocarbon mixture was introduced into a Matheson-Cook bomb calorimeter over 30 c.c. of water and ignited in oxygen to produce sulphur trioxide, which dissolved. The sulphuric acid thus formed was isolated from any other acids, such as CO_2 and HNO_3 , which might be present by precipitation as benzidine sulphate, which was then hydrolysed at 50°C. , and the acid solution titrated with standard potassium hydroxide.

Gas Analysis.

Hydrogen, carbon dioxide, and the hydrocarbons were determined using the Bone and Wheeler apparatus.

Sulphur dioxide in regenerating gases from the catalyst tube was not estimated, but was detected by a dilute solution of *p*-rosaniline. Hydrogen

sulphide in the gases from sulphur runs was estimated by absorption in 2N aqueous sodium hydroxide and back-titration with standard iodine and sodium thiosulphate solution after acidifying with hydrochloric acid.

CYCLIZATION OF *n*-HEPTANE.

The *n*-heptane used had the following characteristics: refractive index n_D^{20} , 1.38775; density, D^{20} , 0.6836; boiling range, 98–98.5° C.; freezing point, –90.7° C.

Six preliminary runs were made on heptane. Two of these, when an approximately 6 atomic per cent. chromium sesquioxide was used as the catalyst at 500° C., with a liquid-space velocity of 1.3 c.c./c.c./hr., yielded a liquid containing 60 per cent. toluene. In another run using the same chromium catalyst the space velocity was very much lower, but the toluene in the liquid product was still about 60 per cent. This result is in agreement with the results of Groose, Morrell, and Mattox, who used this catalyst and concluded that space velocities lower than about 0.3 c.c./c.c./hr. do not appreciably improve the percentage yield of toluene. The preliminary runs where the lower percentage molybdenum catalyst was used did not show very different results from these for the chromium catalyst. No conclusions on the effectiveness of the catalysts were reached from this, however, because the preparations were not made under strictly identical conditions.

Using the standard conditions referred to above, 250 c.c. of *n*-heptane were passed over the standard molybdenum catalyst at 550° C.

Products: Gas and carbon: the gas was assumed to be a mixture of methane and hydrogen on the basis of other published work, and the carbon was deposited on the catalyst. 93 per cent. of the charge was a pale yellow liquid which analysed:—

Naphthalene	1 per cent.
Toluene	55 per cent.
Unsaturateds	5 per cent.
Heptane	40 per cent.
Overall conversion to toluene = 53 per cent.	

The Effect of a Mild-Steel Catalyst Tube.

Observations on the effect of a mild-steel catalyst tube on the cyclization of *n*-heptane were inconsistent, and are not therefore reported in detail. There are certain general conclusions which can be made, however, from over 100 runs in mild-steel tubes.

- (1) Mild steel effects the cyclisation reaction.
- (2) A new tube enhances the reaction.
- (3) After some time the oxide-sulphide scale must be removed before each run to achieve consistently good results.

Cyclization of Heptene.

Since pure heptenes were difficult to obtain and the present work was concerned mainly with the cyclization of hydrocarbon mixtures, technical heptene was used in the experiments described below.

The technical heptene used had a bromine number of 165 (163 for pure heptene), although the distillation curve indicated only 80 per cent. *n*-heptenes.

285 grams of technical heptene were passed over the molybdenum catalyst under the standard conditions and at 550° C. The products are indicated :—

(1) 5 grams of " tar " was deposited in the catalyst tube, extractable with petroleum ether.

(2) A black deposit on the catalyst was formed which was not extractable with organic solvents and was therefore assumed to be carbon.

(3) 65 litres of gas were produced, a sample of which was analysed.

<i>Gas Analysis</i>	CO ₂	Nil
	Olefines	44 per cent.
	Oxygen	Nil
	CO	6 per cent.
	Hydrogen	10 per cent.
	Paraffins	40 per cent.

(4) 185 grams of dark yellow liquid which was distilled, fractionated and analysed for unsaturateds, aromatics and paraffinic hydrocarbons.

In the analysis of these fractions the absorption train method did not give consistent results even with an additional absorber containing 70 per cent. sulphuric acid to remove most of the unsaturateds. The aromatics produced were difficult to nitrate quantitatively, and the products required recrystallizing. The unsaturateds were therefore estimated from the bromine numbers of the fractions, the aromatics by using these values for unsaturateds, and the paraffins were estimated by difference. These results are summarised in Table II.

TABLE II.
Product from Cyclization of Heptene.

	Fraction, ° C.	Per cent. of liquid product.	n_D^{20} .	Aromatics, per cent.	Unsats., per cent.	Paraffins, per cent.
I	67-86	19	1.4310	20	34	47
II	86-93	18	1.4800	20	34	46
III	93-96	34	1.4550	27	38	35
IV	96-110	16	1.4220	15	39	47
V	110-187	10	1.4740	30	17	53

In the first four fractions the aromatics were toluene and benzene, but in fraction V were probably toluene and xylenes, as the recrystallized nitro-compounds melted at 157° C.

Conversion Data.

Charge to aromatics	14 per cent.
Charge to paraffins	19 " "
Charge to tar, carbon, gas, and loss	38 " "

From a consideration of these results it appears that benzene, toluene, and xylenes were produced and the percentage aromatics in the liquid product was about 22 per cent. There is considerable loss by decomposition in the catalytic treatment of technical heptene, and a spreading of the distillation range of the liquid product is obtained. In Fig. 4 are shown the distillation curves of technical heptene and the product. Some polymerization occurs, and, because this is indicated, the percentage unsaturateds in Fraction V as calculated from the bromine number may be too low. A factor which might account for the low yield of toluene from the technical heptene is that some of this was heptene-3, which would be more stable than the less symmetrical heptenes under the conditions of the reaction. The considerable production of paraffins is surprising, but these are not produced mainly by cracking or by disproportionation, because these saturateds are present in similar proportions in all the fractions. Because of

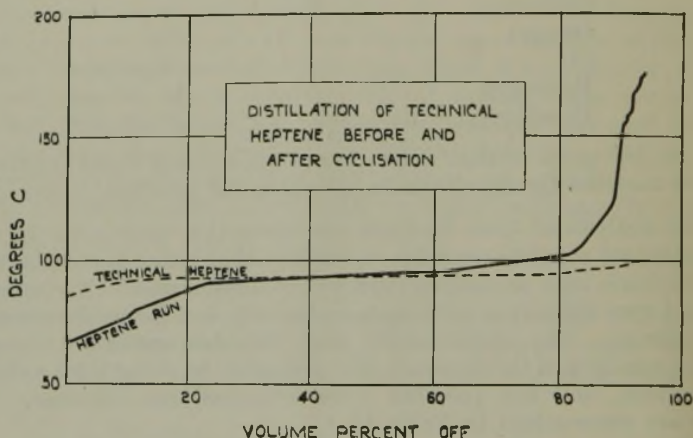


FIG. 4.

this production of paraffins some confirmatory analyses were made. The original heptene was examined further, and found to contain negligible paraffins. A sample of the heptene product was completely brominated, washed free from bromine, and the product distilled from the bromo-compounds and separated into three fractions. The composition of these fractions was then estimated approximately, by an aniline-point method. The percentage paraffins indicated in this way are shown in Table III below.

TABLE III.
Paraffins in converted Heptene.

Fraction, ° C.	Paraffins, per cent.
<100	52
100-103	40
103-114	41

Although these results in themselves cannot give an accurate estimate of the composition of the product, the previous analysis is confirmed, and there

is little doubt that considerable hydrogenation of technical heptene to paraffins accompanied dehydrogenation, cyclization, and cracking under the conditions described.

Heptane-Heptene Mixtures.

The effect of unsaturated hydrocarbons in the substrate on the cyclization properties of paraffins was observed by using various mixtures of *n*-heptane with technical heptene under the standard conditions and at 550° C. The results are shown in Table IV.

TABLE IV.
Cyclization of Heptane-Heptene Mixtures.

Heptene in charge, per cent.	Product.			Aromatics in unsaturateds-free, per cent.
	Unsaturateds, per cent.	Aromatics, per cent.	Paraffins, per cent.	
10	6	24	72	25
19	15	22	59	26
36.8	35	—	—	30
60	52	—	—	33
80.6	72	11	17	39
100	82	10	8	57

In each case carbon and gas were produced in approximately equal quantities, although noticeably more tar was produced for the more un-

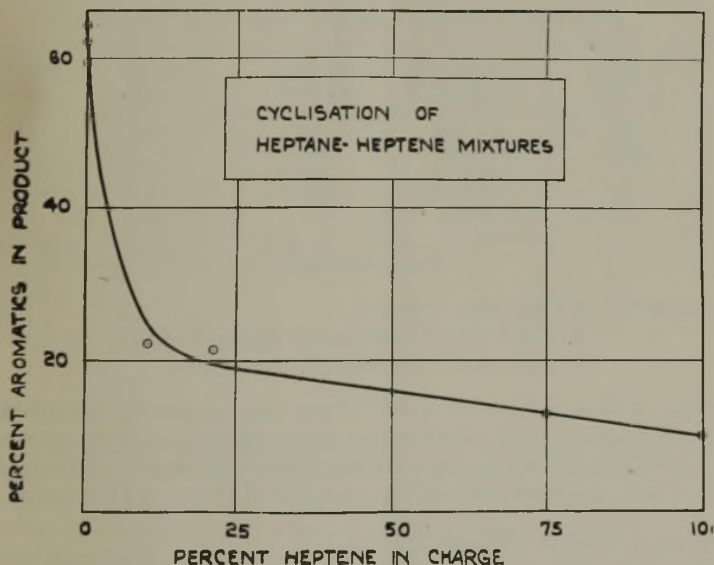


FIG. 5.

saturated feed stocks. When the results are plotted graphically (Fig. 5) it is seen that cyclization decreases with increase in the heptene content of

the charge, although some of the heptene is converted into aromatics or paraffinic hydrocarbons in each case. It appears also that the percentage aromatics in the product falls off rapidly with initial increasing heptene in the feed.

Stability of Toluene under Cyclization Conditions.

Toluene was examined under the conditions of cyclization reactions. A few preliminary runs with A.R. toluene showed a change in colour, odour, and refractive index. 1200 c.c. of pure toluene was therefore prepared, boiling at 110° C. by distillation of A.R. toluene. The toluene was passed over the molybdenum catalyst at 500° C. under the standard conditions described. The horizontal catalyst tube apparatus was used and the run was several days duration, during which time the catalyst was regenerated, and reactivated after every 3 hours.

Products :—The gas produced was analysed but was not measured.

Analysis :— Olefines 11 per cent.
Hydrogen less than 2 per cent.
Paraffins ($n = 1.1$) 85 per cent.

There was some indication of decomposition in the preheater, but the deposit on the catalyst was not extractable with organic solvents, and was therefore assumed to be carbon.

1130 c.c. of a pale yellow liquid was obtained which was distilled using the 25 theoretical plate still, fractionated, and analysed. The analysis is shown in Table V.

TABLE V.
Product from Thermal Catalytic Treatment of Toluene.

	Volume, per cent.	Distillation range, ° C.*	Toluene, per cent.	Unsat., per cent.	Paraffins, per cent.
I	6.4	97–109	78	10	12
II	82.4	109–109	100	0	0
III	2	109–109	100	0	0
IV	6	109–109.5	100	0	0
V	3.2	109.5	—	0	0

* = uncorrected.

Total Analysis : 97 per cent. Toluene
1.2 per cent. Unsaturated Hydrocarbons.
1.2 per cent. Paraffin Hydrocarbons.

Toluene is thus relatively stable under the conditions described, but about 6 per cent. decomposition occurs and a small percentage of unsaturateds is definitely formed. No paraffins were isolated from the liquid product, but both paraffins and olefines were found in the gas produced.

Cyclization of Heptane-Toluene Mixtures.

The effect of the initial aromatic content of the substrate on the aromatic content of the liquid product in the cyclization of hydrocarbon mixtures was investigated for heptane-toluene mixtures.

The runs were all made at 550° C. under the standard conditions described,

excepting that deviations from the liquid space velocity of 0.3 were unavoidable, as the rate of feed varied slightly with the density of the charge. The gas produced was not measured. The results are shown in Table VI.

TABLE VI.
Cyclization of Heptane-Toluene Mixtures.

Toluene in charge, per cent.	Overall heptane converted, per cent.	Liquid product.			
		Per cent. on charge.	Unsats., per cent.	Paraffins, per cent.	Aromatics, per cent.
100	—	69	0.4	0	99
96	0	67	0.5	0	99
92	0	68.3	0.5	0	99
83.5	0	75.8	0.6	0	99
65.6	0	72.1	0.7	16	83
46.0	25.8	77.9	1.6	18	80
24.1	52.6	79.1	1.4	18	81
0	59.5	91.5	4.8	33	62

It appears from the results in Table VI that the total gas, carbon, and tar formation was greater for higher percentage toluene charges. Parallel

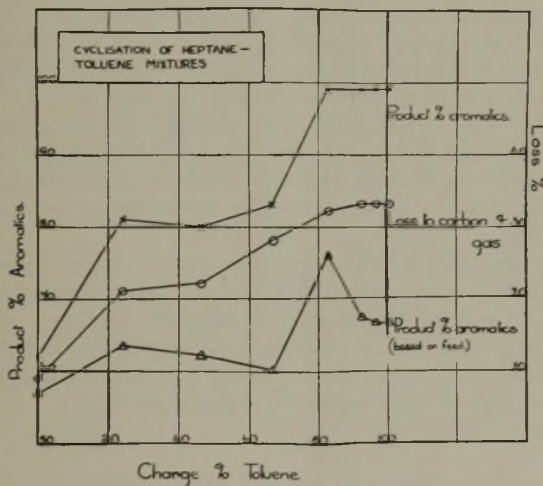


FIG. 6.

with this is the fact that less unsaturateds were formed from these charges. Although the same catalyst was used for the runs and was regenerated and reactivated before each run, the increased loss to carbon, gas, and tar cannot be due to the incomplete removal of carbon and its consequent catalytic cracking activity, as the runs were made in the order shown, and this effect, like that of any deviation in liquid-space velocity (due to the densities of the charges), would be opposite to the results found. Again, although the losses were phenomenally great for the pure toluene charge, the general tendency for increased conversion losses with increasing toluene in the

charge is still shown by the results in Table VI if this run is neglected. From Fig. 6 and Table VI it is apparent that for the most economical conversion of *n*-heptane at 550° C. the least aromatic charge is desirable, while for the production of highly aromatic products, however, there is an optimum range for the aromatics in the charge. It appears, then, that at 550° C. two types of processes are active, cyclization and thermal aromatization or cracking.

Although in the 65.6 per cent. and 83.5 per cent. toluene runs there was no overall conversion of heptane into toluene, since from the general results in Table VI the aromatics are lost to gas, carbon, and tar rather more readily than the paraffins, it seems that heptane was converted into toluene in predominantly aromatic mixtures.

Cyclization of 2 : 2 : 4-Trimethyl Pentane.

Hoog, Verheus, and Zuiderweg³⁰ compared the cyclization of various paraffins over pilled Cr_2O_3 catalyst with contact times of 18–24 seconds and a reaction temperature of 465° C. Eighteen hydrocarbons were examined, and of these, *n*-pentane, 2-methyl pentane and 2 : 2 : 4-trimethyl pentane were not appreciably aromatized, although in each case there was considerable olefine formation, but no notable cracking. From distillation data and the composition of reaction gases it was deduced that the formation of higher-molecular-weight compounds occurs with these base materials which are not appreciably aromatized (*e.g.*, 2 : 2 : 4-trimethyl pentane). It was also generally concluded that paraffins with structures not readily permitting the formation of a six-membered ring are not appreciably aromatized, and that, since there are formed from paraffins only those aromatics which would be expected on this basis, then under the given conditions chromium sesquioxide does not effect isomerization of the carbon skeleton, although some lower aromatics might be formed as a result of cracking reactions.

For the aromatization of many hydrocarbon mixtures these conclusions impose definite theoretical restrictions, and the thermal catalysis of 2 : 2 : 4-trimethyl pentane was therefore investigated further. Although the following experimental work was carried out merely to find the conditions of formation of aromatics, no single process was being studied, and no gas analyses were made, certain interesting facts were found.

Experimental.

(1) Pure 2 : 2 : 4-trimethyl pentane twice redistilled from the Röhms-Haas product was passed over the molybdenum catalyst at 550° C., using a mild steel catalyst tube and a liquid catalyst-space velocity of about 0.3 c.c./c.c./hr. A pale yellow liquid product was obtained, 50 per cent. of the charge. There was considerable gas and carbon production.

Analysis of Liquid Product.

Aromatics	50 per cent.
Paraffins	47 " "
Naphthalene	2 " "
Unsaturateds	1 " "

There was, then, a conversion of 25 per cent. of the charge into aromatics. The nitro-compounds prepared from the aromatics at 100° C. melted at 179° C. That these were aromatic compounds was shown by reduction to amines, diazotization, and coupling with β -naphthol. Oxidation of the original hydrocarbon mixture with alkaline permanganate yielded some phthalic acid, m. p. 190° C. The aromatics in the product were then a mixture of xylenes, *o*-xylene being identified.

(2) 166 c.c. of pure 2:2:4-trimethyl pentane were passed over a 6 atomic per cent. chromium sesquioxide alumina catalyst at 450° C. in a mild-steel catalyst tube. The catalyst was prepared from chromium nitrate and reduced in hydrogen. The liquid catalyst space velocity was 0.33 c.c./c.c./hr. 18.5 litres of gas and a pale yellow liquid (89 per cent. of charge) were produced.

Analysis of Liquid Product.

Aromatics	1.9 per cent.
Unsaturateds :	15.1 " "
Paraffins (by difference) :	82 " "
Gum (including some naphthalene) : less than	1 " "

Considering the nitro-compounds obtained the aromatics present were probably mixed xylenes together with some benzene. Identification by oxidation with alkaline permanganate was not successful.

The unsaturateds were not identified. The aromatics and unsaturateds were then removed by absorption in 98 per cent. sulphuric acid and the residue examined; distillation indicated that the greater part of the residue boiled below 84° C. and that there was a 10 per cent. fraction at 74° C. The refractive indices of various arbitrary fractions were found, and some are shown in Table VII. From these results it appeared that isomerization

TABLE VII.

Fraction, ° C.	Per cent. of aromatics and unsats.-free product.	n_D^{20} .
(1) { 64	15	1.3900
64-85°	35	1.3919
85-98	20	1.3945
Residue	6.5	1.4362
Original mixture	100	1.3979
(2) { 40	6	1.3935
40-50	2	
50-74	38	
74	26	—
74-98	18	1.3948
Residue	—	1.4185

to more highly branched compounds had taken place. However, although 98 per cent., sulphuric acid was shown not to affect "*iso*-octane" alone, it was found that under the usual conditions washing with acid of this strength does not remove unsaturateds completely, and that the effect of acid treatment in the presence of such unsaturateds could account completely for the results found.

The production of both lower- and higher-molecular-weight compounds was indicated, and further evidence for the former was obtained by determination of molecular weights of two fractions from a further distillation. This is shown in Table VIII.

TABLE VIII.

Sample.	Molecular weights.	
	Found.	Theoretical.
Original 2 : 2 : 4-Trimethyl pentane	112	114
70-90° C. Fraction	102	100 for C_7H_{16}
90-112° C. Fraction	112.1	114 for C_8H_{18}

From the above it would appear that considerable aromatization of 2 : 2 : 4-trimethyl pentane is possible under certain conditions, but is accompanied by very considerable cracking.

Benzene-2 : 2 : 4-Trimethyl Pentane Mixture.

From thermodynamic considerations it has been shown that the reaction of benzene and 2 : 2 : 4-trimethyl pentane to give toluene and the elements is permissible in the temperature range of the cyclization reaction. From this indication and from a consideration of the cracking possibilities, alkylation of the aromatic ring with a dehydrogenation catalyst might take place under suitable conditions.

A mixture of 55.8 per cent. pure thiophen-free benzene and 44.2 per cent. of pure 2 : 2 : 4-trimethyl pentane was passed over the molybdenum catalyst at 550° C. under the standard conditions described above. The product was distilled, fractionated and analysed.

Products.

10 per cent. of charge as gas, carbon, and loss.

90 per cent. of charge as a colourless liquid with a distillation range of 74-110° C. (The distillation range for the charge was 80-95° C.)

Analysis.

The analysis of the product is shown in Table IX.

TABLE IX.

Analysis of Fractionated Liquid Products from Benzene-iso-octane Run.

	Fraction, ° C.	Volume, per cent.	Refractive index, n_D^{20} .	Unsat., per cent.	Aroms., per cent.	Paraff., per cent.	M. p. of nitro- compounds, ° C.
1	74-80	8	1.4905	98	58	32	88
2	80-83	45	1.4697	18	50	32	86
3	83-90	26	1.4554	29	35.1	35.0	87
4	90-110	6	1.4700	10	49	4	179

The aromatics in fractions 1, 2, and 3 were assumed to be benzene from the melting points of the isolated nitro-compounds. The aromatics in

fraction 4 were probably *o*- and *m*-xylenes. The nitro-compounds isolated from this fraction were reduced, but the amines could not be isolated satisfactorily. On diazotization, however, a dye was obtained by coupling with alkaline β -naphthol. Neither the diazo-dye nor the amine hydrochloride could be crystallized satisfactorily for characterization.

The total liquid product had the following composition.

48 per cent. aromatics.
40 per cent. benzene.
8 per cent. mixed xylenes.
35 per cent. paraffins.
15 per cent. unsaturated hydrocarbons.
0.1 per cent. naphthalene.

Thus both the percentage benzene and 2:2:4-trimethyl pentane had decreased. The reaction must have involved the benzene present, since benzene alone under the same conditions was not changed. Since, however, the formation of xylenes was found when *iso*-octane alone was treated under the same conditions, the possible alkylation of benzene with other hydrocarbons by contact catalysis is not decided either way by these results. Benzene alone was stable under the same conditions as shown by the experiment below.

Benzene Run.

Pure thiophen-free benzene was treated under the standard conditions described at 550° C.

Products.

Gas : 1 per cent. of charge. The gas did not contain unsaturates.

Carbon : A light deposit on the catalyst unextractable with organic solvents. This deposit was noticeably less than in other runs.

Liquid : 98 per cent. of the charge as a colourless liquid boiling at 80-81° C.

Bromine number = 0

$$n_D^{20} = 1.5012, 1.5013$$

Original benzene : $n_D^{20} = 1.5011, 1.5010$.

Discussion.

The production of the considerable proportion of paraffinic hydrocarbons during the cyclization of technical heptene is rather surprising. Taylor and Turkevich² using small quantities of gel catalyst (15 g.) found that the percentage paraffins produced in the cyclization of heptene-1 dropped from 13 per cent. at 424° C. to 2 per cent. at 474° C. Since the paraffins are in similar proportion in all fractions of the product, it appears that they are produced by catalytic hydrogenation during the dehydrogenation reactions. Thermodynamically the conditions were favourable for heptene production, and the fact that this was realized to a considerable extent suggests that the conditions approached hydrogenation equilibrium conditions closely.

In Fig. 5 for heptane-heptene mixtures it is apparent that aromatization of heptane is decreased considerably by small quantities of technical heptene, and the initial presence of unsaturated compounds in the sub-

strate thus considerably limits the efficacy of the cyclization reaction. This seems to be in accordance with the discovery² that cyclization catalysts are poisoned irreversibly by ethylene. The conversion of heptane into toluene even in predominantly aromatic mixtures favours the assumption made by some workers that paraffins can compete effectively with aromatics for the catalyst surface under cyclization conditions.

Much more experimental work is necessary before any general conclusions can be made on the isomerization of 2 : 2 : 4-trimethyl pentane by cyclization catalyst, and the work is being continued. It seems desirable that more attention should be paid to the paraffinic portion of the products and that the formation of aromatic hydrocarbons should not be taken as the only indication of isomerization. For this purpose much greater volumes of the substrate must be used than hereto and attention given to the qualitative nature of the products.

Cyclization of Mixtures containing Sulphur Compounds.

Preliminary investigation was carried out on mixtures containing varying proportions of sulphur compounds from two aspects. The resistance to poisoning by sulphur and the desulphurization capacity of the cyclization catalysts was tested together with the effect on the chemical composition of the products from sulphur containing charges.

Experimental.

Molybdenum and chromium, forming stable sulphides, might be expected to act as desulphurizing catalysts. Indeed, molybdenum trisulphide has been claimed as a desulphurizing catalyst (B.P. 315,439) when supported on charcoal and other carriers. The trisulphide was therefore precipitated on active charcoal and dried at 110° C. With this catalyst a 30 per cent. reduction in total sulphur for a single pass was obtained running a benzole fraction with hydrogen at 300° C. On the basis of several experiments it appeared that for best results the catalyst should be treated with hydrogen sulphide at intervals. A catalyst was prepared by depositing MoS_3 and Co_2O_3 on pumice in their molecular proportions and treating with hydrogen sulphide at 300° C. At this temperature reductions in total sulphur of a benzole fraction of 14 per cent. when using a liquid catalyst space velocity of 1.9 c.c./c.c./hr. and 26 per cent. when using 0.13 c.c./c.c./hr. were obtained. In this preliminary work hydrogen was passed with the feed to reduce the sulphur compounds to hydrogen sulphide. When considering cyclization catalysts, however, it was apparent that a new principle might be involved, since the hydrogen required to reduce the sulphur compounds could be supplied, under suitable conditions, by the cyclization reaction itself. In order to test the capacity of the cyclization catalysts for desulphurization and their resistance to sulphur poisoning in a suitable time, a search was first made for the highest percentage sulphur in the charge which could be desulphurized efficiently. The conditions used were very similar to the standard conditions described above, deviations from these being due to variations in the feed-rate probably caused by increasing density of the feed with increasing content of carbon disulphide. This material was used in a 110–120° C. benzole fraction to give charges of various sulphur contents.

In Table X the experimental results are shown and in Fig. 7 are expressed graphically.

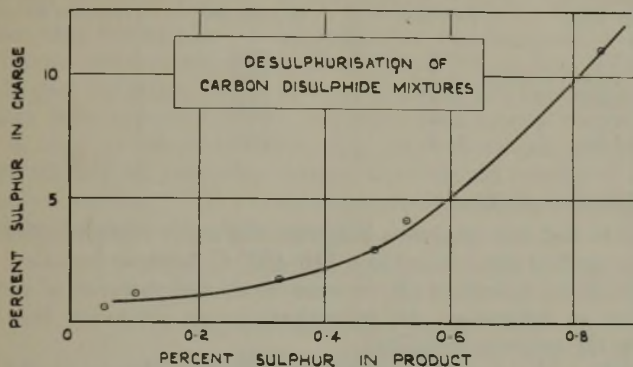


FIG. 7.

TABLE X.

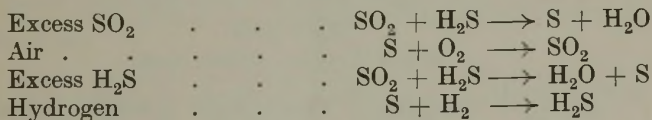
Desulphurisation of Carbon Disulphide Mixtures.

Temperature : 550° C.

Contact Time : 35-40 seconds.

Run no.	Input, c.c.	Feed-rate, c.c./min.	Product, c.c.	Gas produced, c.c.	Sulphur in feed, per cent.	Sulphur in liquid product, per cent.	Desulphurization, per cent.
47	40	1	33	3200	1.14	0.10	91
48	35	0.875	32	2600	1.7	0.33	80
49	35	0.875	30	2400	3.0	0.49	84
50	34	0.875	30	2200	4.2	0.53	87
51	35	0.875	30	3200	11.2	0.85	93

The catalyst was regenerated with air before each of the runs above until no more sulphur dioxide (detected with *p*-rosaniline) was evolved. In this way, sulphur dioxide was found to be present even when air had been passing for 3 hours. When hydrogen was passed to reduce the oxide, H₂S was formed, indicating that sulphur was combined on the catalyst. H₂S and SO₂ were not estimated in the presence of each other, for it was assumed that the reactions shown would go to completion above 500° C.



The products of runs 47-51 were examined for aromatics and unsaturates. In Table XI it can be seen that the percentage unsaturates increases with increasing sulphur content of the charge. Although this increase is small, it is significant that the aromatic content of the product falls over a similar range. The true conversions were certainly greater than indicated in Table XI because the experimental losses were great as small volumes of the order of 100 c.c. were used.

TABLE XI.

Run no.	Charge S, per cent.	Per cent. unsats. in product.	Per cent aromatics in product.	Overall percentage conversion to aromatics.
47	1.14	12.1	80.8	2
48	1.70	14.2	78.3	7
49	3.00	13.8	79.8	3
50	4.20	15.0	76.7	1
51	11.20	17.4	76.7	1

Catalyst Desulphurization Tests.

In order to test the catalyst a long run was made charging 25.3 per cent. sulphur (as carbon disulphide) in a 110–120° C. benzole fraction.

The conditions described above were used, and samples of the product were taken at intervals. At somewhat longer intervals the hydrogen sulphide in the gas was estimated.

The catalyst was then reactivated and further charge passed. It was obvious that copious evolution of hydrogen sulphide was taking place in the second stage, but no estimations of the gas could be made. During the reactivation, however, considerable sulphur dioxide was evolved when air was passed over the catalyst.

In Tables XII and XIII are shown the results for the first and second stage runs.

TABLE XII.
Desulphurization—First Stage.

Run no.	Duration, mins.	Yield of liquid products, c.c.	Sulphur in liquid product, c.c.	Sulphur in gas, g./hr.
52	60	22	0.91	—
53	120	48	0.87	0.50
54	180	113	2.28	—
55	245	180	3.60	0.49
56	335	250	—	—
57	395	340	3.92	—
58	425	380	5.56	0.17
59	520	510	7.00	—
60	525	515	—	—
61	690	691	—	0.10
62	840	861	7.88	—
63	910	941	7.54	—
64	920	951	—	—
65	1040	1051	8.36	0.13

TABLE XIII.
Desulphurization—Second Stage.

Run no.	Duration, mins.	Yield of liquid product, c.c.	Sulphur in liquid product, per cent.
66	60	35	6.61
67	150	95	7.96
68	270	221	6.30
69	315	277	12.8
70	395	372	—
71	505	—	10.1
72	520	384	11.9

Since sulphur dioxide was produced in the reactivation process, and as molybdenum sulphides are very stable, it is probable that some sulphur was sorbed by the catalyst carrier. The tests made were extremely severe, and the fact that the catalyst desulphurized to the extent of 60 per cent. after a 17-hour continuous run, without reactivation, and without any added hydrogen, indicates that it is very stable to sulphur, although from these results it is expected to be progressively poisoned over very long periods. It may be found, however, that when lower-percentage sulphur charges are treated no poisoning occurs, and that no sulphur is absorbed on the catalyst carrier. The second-stage experiment shows (Fig. 8) that the poisoning observed is in part reversible.

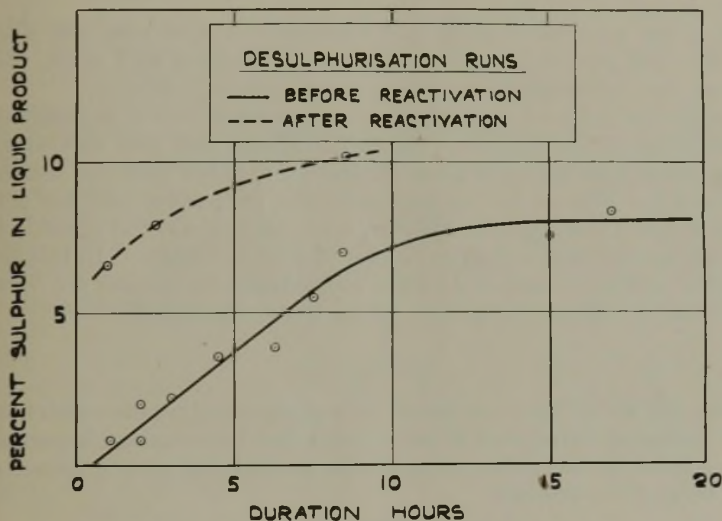


FIG. 8.

Thiophen Run.

A 1 per cent. sulphur (as thiophen) mixture was made in hexane and run over a new catalyst using the conditions of previous runs. The results are shown in Table XIV.

TABLE XIV.

Charge : 198 c.c. 1% sulphur (as thiophen) in hexane.

Product : 111 c.c. in three fractions : average percentage sulphur = 0.34 per cent.
28 litre of gas.

Run no.	Vol. liquid product, c.c.	Duration of run, hrs.	Percent. S. in liquid product.	Percent. benzene in liquid product.
78	31	—	0.10	60
79	30	1	0.53	60
80	50	1	0.38	51

Thiophen is thus much more difficult to remove under the conditions stated than is carbon disulphide, but the results indicate that the catalyst

is stable to sulphur in the charge when in the form of carbon disulphide or thiophen, and effectively desulphurizes in both cases.

DISCUSSION.

Although the work reported here is not extensive and no light is thrown on the processes of poisoning and desulphurization, an important principle is indicated—that of complex catalysts where the complexity is due not to the catalyst but to the substrate itself. It is clear that with a molybdenum catalyst the processes of cyclization and desulphurization proceed together. It has been observed before⁴³ that molybdenum sulphide is an active catalyst for hydrogenation-dehydrogenation, as is molybdenum oxysulphide.⁴⁴

When the spent catalyst from the desulphurization runs was analysed, however, the proportion of Mo to S was 0.81 atoms to 1 atom, hence it appears that the catalyst was a mixture of oxide and sulphide.

The greater resistance of thiophen to decomposition is probably due to the stability of the thiophen ring itself, but the fact that this compound is decomposed under cyclization conditions, together with the possibilities of conversion of near boiling non-aromatics to benzene and the stability of the latter under these conditions, serve to indicate the possible use of cyclization catalysis for the production of pure aromatics. In this connection it is worthy of note that some nitrogenous compounds are converted into ammonia and hydrocarbons during the cyclization reaction.⁴³

CONCLUSION.

Table XV shows the most important experimental results which have not been tabulated above, and it can be seen that naphthalene formation was quite general in the cyclization reactions studied and usually formed about 1 per cent. of the product.

TABLE XV.

	Feed.	Catalyst.	Temp., ° C.	Liquid catalyst space velocity, v./v./hr.	Loss, gas, carbon, etc., per cent.	Products: percentages on charge. (Liquid.)			
						Aroma- tics.	Unsat.	Paraf- fins.	Naphtha- lene.
1	Benzole	Copper chromite	500	0.3	—	Increase of 8%	Increase of 9%	—	1
2	n-Heptane	Mo ₂ O ₃ on alumina	550	0.3	7	53 (toluene)	4	39	1
3	Technical heptene	Mo ₂ O ₃ on alumina	550	0.30	38	14	19	29	—
4	Toluene	Mo ₂ O ₃ on alumina	550	0.31	3	95 (toluene)	1-2	1-2	—
5	2:2:4-Trimethyl pentane	Mo ₂ O ₃ on alumina	550	0.30	50	25	1	24	1
6	2:2:4-Trimethyl pentane	Cr ₂ O ₃ on alumina	450	0.33	11	1-2	12-14	73	1
7	Hexane with 1 per cent. thiophen	Mo ₂ O ₃ on alumina	550	—	—	50	—	—	—

Cr₂O₃ from chromic acid, on floridin as carrier, showed negligible activity, whereas when the sesquioxide was prepared from chromium nitrate, using the same carrier, the aromatics and unsaturateds in a hydrocarbon mixture were increased by 16 per cent.

Copper chromite and molybdenum sulphide on various carriers were active, but the introduction of activated alumina increased the activity of these and other catalysts considerably. Activated alumina alone was also active.

Various mixtures were passed over a molybdenum-alumina catalyst, and it was found that *n*-heptane is more easily aromatized than technical heptene. The reactions of other mixtures are discussed, and *o*-xylene was identified from the aromatization of 2 : 2 : 4-trimethyl pentane. At 550° C. 2 : 2 : 4-trimethyl pentane was converted into 25 per cent. aromatics, but this conversion was accompanied by extensive cracking.

Desulphurization and aromatization of benzole fractions were found to be technically inseparable processes. The activities of various catalysts for desulphurization were studied. Molybdenum sulphide showed greater activity than chromium sulphide, except when the former was prepared outside the catalyst tube.

In general, the cyclization of hydrocarbon mixtures results in a spreading of the distillation curve, formation of gas and carbon and an increase in aromatic and unsaturated hydrocarbons. At the same time hydrogenation reactions take place. The product from such a reaction will therefore depend on the conditions of the reaction and on the nature of the substrate. By the choice of suitable conditions, and by varying the composition of the substrate, it is possible to achieve several different reactions at the same time, using a single catalyst.

In a later paper the continuation of this work will be described, and the significance of some of the results may be seen in a different perspective.

The author wishes to express his appreciation for the interest and encouragement shown by the late Professor A. W. Nash and by Dr. T. G. Hunter of this Department.

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SPRING TENSION BALANCE FOR C.F.R. BOUNCING PIN.*

By P. DRAPER.†

INTRODUCTION.

AN instrument was designed in 1939 by D. M. Clement, of the Shell Laboratory, London, for accurately determining the tension of the leaf-springs and plunger-spring on the C.F.R. adjustable-leaf-type bouncing-pin, the standard instructions for setting being inadequate, particularly when testing high-octane fuels.

After consideration by the Knock Rating of Aircraft Fuels Panel Subcommittee of the Institute of Petroleum detail alterations were made, and the final apparatus proved so successful that it has been employed for some time in almost every C.F.R. installation in the United Kingdom and in many laboratories overseas.

DEVELOPMENT.

The A.S.T.M. instructions for the setting of the old-type pin gave the limits of the free deflections, due to a permanent set of the lower and upper leaf-springs. These deflections were quoted in the A.S.T.M. procedure in sixty-fourths of an inch, and their limits were $\frac{3}{64}$ — $\frac{4}{64}$ inch for the lower leaf-spring and $\frac{6}{64}$ — $\frac{7}{64}$ inch for the upper leaf-spring. The plunger-spring tension must be within 1.0–1.25 lb.

The above deflections were measured with an initial contact gap of 0.005 inch and the pin then removed.

For simplicity, these deflections are now designated in thousandths of an inch with the gap just closed when the pin is in position, thus :—

The limits for the lower leaf are . . . 0.042–0.057 inch

The limits for the upper leaf are . . . 0.099–0.114 inch

It has been experienced that the deflection-load characteristics of all springs supplied are not similar. Springs in service become buckled and also lose their elasticity; new springs have not precisely similar dimensions and elasticity. Consequently there has been no definite knowledge or control of the forces of the springs acting on the pin. This instrument can determine true spring tensions in grams while the springs are in position.

The deflection-load characteristics of a number of springs gave the

* Paper received 18th July, 1942.

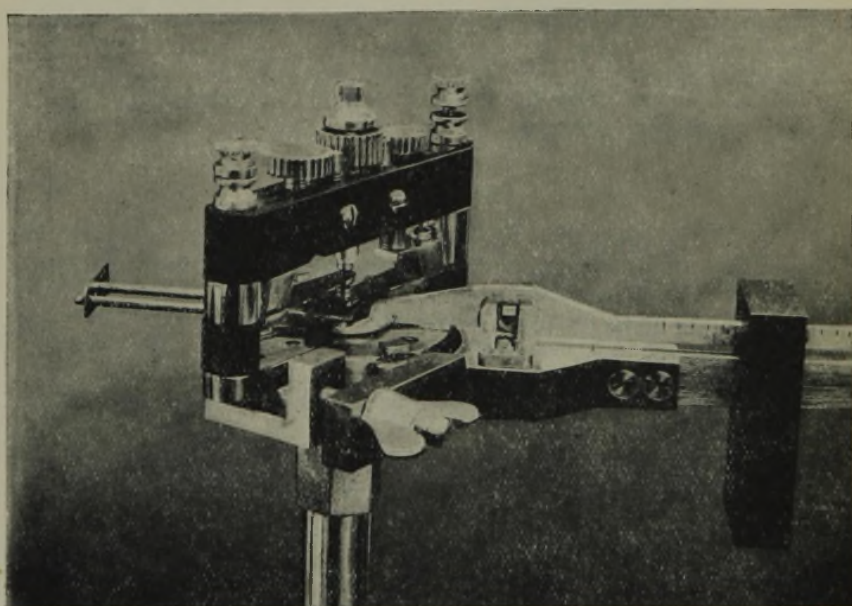
† Asiatic Petroleum Co., Ltd.

following average figures for the forces in grams when the springs were deflected to the extent given by the A.S.T.M. upper and lower limits.

		Force in grams.
Lower leaf-spring deflection . . .	0.042 inch	180
	0.057 "	245
Upper leaf-spring deflection . . .	0.099 "	380
	0.114 "	440
Plunger pressure	1 lb.	454
	1.25 lb.	568

THE INSTRUMENT.

The instrument is simply a beam balance 9 inches in length, pivoted on a knife-edge (see drawings and photograph). The assembly is clamped to the flange of the bouncing-pin body, and made rigid by the tightening of



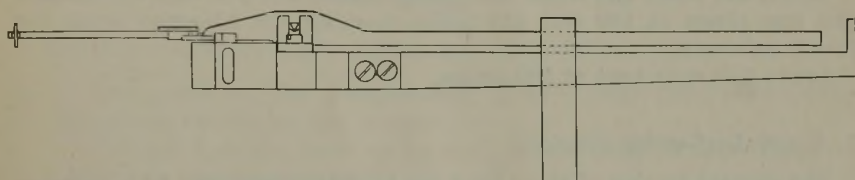
a thumb-screw. No part of the pin need be dismantled for this purpose. (The bouncing-pin assembly may remain in the engine or it may be held vertically in a vice.)

The inner end of the beam is forked, and bears at two points upon the underside of a thin clamp, which is attached to the tip of the pin protruding from the pin body. An imaginary line through the two bearing points passes through the vertical axis of the pin, thus a true value of the forces required to deflect the springs may be determined. A jockey weight on the outer arm balances the combined force of the spring to be tested and the weight of the pin and collar. The beam is calibrated from 150 to 570

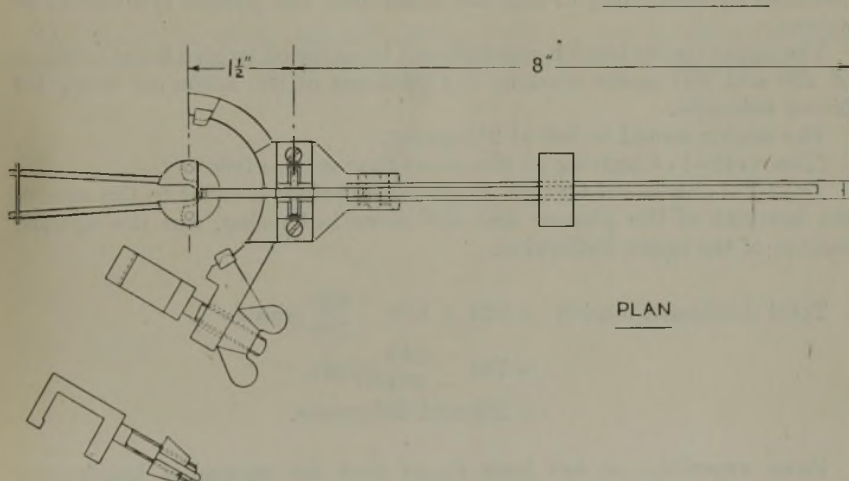
grams at intervals of 10. A reading may be made to half a division, which is the limit of accuracy. (The average weight of the pin and the small clamp have been allowed for in the calibration of the beam.)

APPLICATION.

It should be appreciated that the lower leaf-spring provides a downward force restraining the movement of the bouncing-pin, and thus causing the contacts to close only during detonating conditions. The upward force of the upper leaf-spring and the downward force of the plunger provide a nett "buffer" force for the bouncing-pin and lower leaf-spring to bounce against. It is this nett "buffer" force which determines the duration of electrical contact of the contact points, and therefore the sensitivity of the circuit.



SIDE ELEVATION



PLAN

After the bouncing-pin assembly has been dismantled for cleaning and re-assembled, the spring-tension should be checked in the following sequence :—

1. *Plunger Tension.*

Swing aside the two leaf-springs by loosening their mounting screws at the ends of the lower cross-bar.

Raise the pin until it touches the plunger, and attach the pin-clamp

to the pin so that there is $\frac{3}{16}$ inch between its under face and the bouncing-pin body.

Mount the beam and adjust the plunger tension to 455 and 570 grams, marking the positions of the adjusting screw for future reference.

Leave the plunger set at 530 grams.

(The figure on the beam-scale flush with the inner surface of the jockey weight will give the force in grams.)

2. *Lower Leaf-spring Tension.*

Reassemble the two leaf-springs, seeing that they are correctly aligned, and set the contact gap to approximately 0.001 inch.

Attach the pin-clamp to the pin so that there is $\frac{3}{16}$ inch between its under face and the bouncing-pin body.

Mount the beam and adjust the spring-tension screw so that the contact gap just closes at 180 and 245 grams marking the adjusting screw for future reference.

Leave this spring set at 180 grams.

3. *Upper Leaf-spring Tension.*

The upward tension of this spring can be determined only by measuring the combined force of all the springs, and thence by calculation. This is obtained by continuing to load the beam until the plunger is about to be moved.

The upper spring tension-screw should be adjusted to give beam loadings of 270 and 330 grams marking the positions of the adjusting screw for future reference.

The setting should be left at 310 grams.

(The method of arriving at the above figures is as follows :—

The total downward tension of the three springs is equal to the sum of the tensions of the plunger and the lower leaf-spring, less the upward tension of the upper leaf-spring.

$$\begin{aligned} \text{Total downward tension} &= 530 + 180 - 440 \text{ grams.} \\ &= 710 - 440 \\ &= 270 \text{ and } 330 \text{ grams.} \end{aligned}$$

From experience it has been found that for maximum knockmeter sensitivity the nett balancing force of the plunger and upper leaf-spring should be about 130 grams. Therefore 530 and 400 grams have been chosen for the initial setting of these springs. The total downward tension is thus $710 - 400 = 310$ grams.)

4. Remove the spring-tension apparatus and set the contact gap to 0.003 inch (its limits being 0.003–0.005 inch.)

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

Subsequent Setting.

A 55-60 knockmeter reading should be obtainable under standard conditions of operation by *very slight* adjustment of the contact gap within the limits specified above.

For testing high-octane fuels it may be necessary to increase the downward tension of the lower leaf-spring to a maximum of 245 grams. See Institute of Petroleum Standard Methods 1942. (For testing by the 17° Motor Method it may be necessary to increase the tension to 300 grams. See *J. Inst. Pet.*, May 1941, Vol. 27, p. 191).

It should not be necessary to alter the settings of the plunger or upper leaf-spring, but the sensitivity of the knockmeter depends on these relative settings. (Provided that the lower leaf-spring is exerting sufficient downward force to prevent the recording of "combustion pressures".)

NOTES.

The following approximate figures may be useful :—

One notch on the plunger-screw is equivalent to approximately 15 grams tension on the plunger.

One notch on the lower spring-screw is equivalent to approximately 10 grams tension on the pin.

One notch on the upper spring-screw is equivalent to approximately 10 grams tension.

Care should be taken that the reading of the number of notches of turn of the upper spring-screw is not a false one on account of the backlash.

OBITUARY.

JAMES ROMANES.

IN the sudden and premature death of James Romanes at the early age of 56, Great Britain loses one of its most talented and respected geologists and authorities on oilfield geology. Following his education at the Edinburgh Academy, he proceeded to Christ's College, Cambridge, where his inherited inclinations and outstanding abilities were concentrated on geology, and he there obtained his B.A. (Natural Science Tripos, 1st Class) in 1908, and Natural Science Tripos, Part 2, 1st Class Geology, in 1909. He was Harkness University Scholar in 1911 and became an M.A. in 1912. For a time he remained at the University as lecturer and coach in geology, whilst engaged on research work, thereby becoming acquainted with many students who sought his advice and guidance when building a career and later acquired distinction. One of his earliest associations with oil was on an expedition that had for its object the determination of oil prospects in the Eastern Andean foothills of Bolivia, a task which involved two years' absence in remote and inhospitable country.

The European War of 1914-18 caused a break in his professional activities, for he at once joined up, and obtained a commission in a Border regiment that was eventually drafted to Gallipoli. At Suvla he was gravely wounded when leading his company in an attack on Turkish positions, and was reported killed; indeed, his obituary notice appeared in *The Times*, and his family went into mourning. On recovering from his wounds he accepted a post with the Royal Flying Corps, where his scientific accomplishments were quickly recognized and applied in investigations of a confidential nature. When peace was proclaimed and he secured his release from the Army with the rank of Colonel, he renewed his connection with the petroleum industry, and became a partner in the firm of A. Beeby Thompson and Partners, where his great organizing, scientific and commercial abilities found full scope in directing and supervising topographical and geological surveys connected with petroleum and water projects. Romanes was closely identified with oil exploration in Trinidad, Barbados, Germany, Portugal, Irak and Syria, and amongst his various foreign excursions was one to Iceland and another to Teneriffe. He contributed articles to the *Encyclopaedia Britannica*, and sought by many Press articles to attract public interest in the London Water Supply by proposals to re-charge the depleted London Basin with water from the Thames at times of flood.

Romanes had served on the Councils of the Geological Society and Institute of Petroleum, and he was very actively associated with the Mining Club. He was a gifted and lucid speaker and writer, and in debate he was blunt and forceful, but always willing to concede a point which merited respect. His great charm of manner and fund of dry humour attracted many friends, and at West Byfleet his ready willingness to help in any social or patriotic movement led him to take a keen interest in golf and to initiate the Home Guard movement in his district.

A. B. T.

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Geology and Development.

760.* Drilling in United States Levelling Off at Reduced Rate. Anon. *Oil Wkly*, 11.5.42, 105 (10), 33.—The daily average rate of well completions in April was only slightly below the March rate, and nearly as many wells were drilling or rigging on 1st May as on 1st April. 1366 wells were completed in the four weeks ended 25th April, 1942, a daily average of 48.8, compared with 50.2 for March.

North Louisiana, Mississippi, New Mexico, West Texas, the Texas Panhandle, New York, Pennsylvania, and West Virginia have had more completions during the first four months of 1942 than during the corresponding period of 1941. 1999 wells were drilling on 1st May, 1942.

Data are tabulated by States and districts concerning the drilling activity in April 1941, March and April 1942, the cumulative completions during the first four months of 1942, and the activity on 1st May, 1941, and 1st April and 1st May, 1942.

G. D. H.

761.* Florida Leasing Activities Showing Increase. J. G. Heyck. *Oil Wkly*, 18.5.42, 105 (11), 41.—Much of the acreage under lease in Florida was leased late in 1939 and early in 1940. At present 3,605,000 acres are under lease, and they lie in five general areas: (1) Panhandle or West Florida (948,500 acres); (2) west flank of Ocala uplift (780,100 acres); (3) east flank of Ocala uplift (180,000 acres); (4) south-south-west flank of Ocala uplift (666,400 acres); (5) Everglades basin (1,030,000 acres).

In October 1941 marine leases were granted along the west and south coasts of Florida, and some 12,000,000 acres have been taken up on eighteen-month geophysical options. G. D. H.

762.* Typical Oil-field Structures ; Complexly Faulted Dome, Eola Field, Avoyelles Parish, Louisiana. Anon. *Oil Gas J.*, 21.5.42, 41 (2), 50.—The Eola field is along a trend associated with wedging sands, but it lies some distance from the old shoreline. The beds thicken towards the Gulf, and the coastwards dip is broken by salt domes and by faulted domes not definitely known to be associated with salt, which is generally considered to be Jurassic in age. The faulted domes may be due to compaction of soft formations around salt cores, or to adjustments in a subsiding wedge without being localized by salt or other resistant plugs.

Eola is a roughly oval dome on a broad, gentle regional nose on a seaward-dipping monocline. Most of the faulting cannot be traced above the Vicksburg, due to rapid facies changes rendering correlation difficult. The throw of the faults decreases upwards. The northerly closure dies out in the Cockfield.

The Cockfield and Sparta sands carry oil, but the main production is from the Wilcox. The different fault-block segments behave differently and have different bottom-hole pressures, although the water-level is the same.

The Cockfield is predominantly sandy and of near-shore or lagunal origin, with much carbonaceous matter which may be the source of the oil. The Wilcox is a black, silty, lignitic shale of shallow marine or lagunal origin.

The Wilcox production is not limited to the upper part of the formation, and as the Wilcox locally is several thousand feet thick, the possibility of picking up local shoreline trends is very great. The same is true of the Sparta, Cockfield, and still higher horizons.

Surface and subsurface geology are of little value in locating these deep-seated, complexly faulted domes. The reflection seismograph with the guidance of regional geology is responsible for most of the discoveries made so far. G. D. H.

763.* Results in South Caesar will Influence Carrizo-Wilcox Play. F. L. Singleton, *Oil Gas J.*, 21.5.42, 41 (2), 70.—The first commercial Carrizo production of South-west Texas has recently been found just south of the old Caesar field. Three wells have revealed the existence of an important reserve, and a second 50-ft. sand has been found. Production is spread over a mile in a north-east-south-west direction on an elongated structure parallel to the Caesar field fault. The discovery well was completed at 6552–6557 ft. for 127 bbl./day of 42-gravity oil on $\frac{1}{4}$ -in. choke.

The second sand, showing salt water and a little oil in the discovery well, is 105 ft. deeper. It was logged as carrying gas-distillate in a second well.

The discovery well seems to be near the apex of the structure. Dry wells have been drilled which appear to limit the field to the south-east.

The area was leased on the basis of subsurface work, checked by geophysics.

The discovery has led to special attention being paid to other old Pettus sand-fields, many of which are practically depleted, but which can be regarded as favourable prospects in the light of recent developments. Deeper drilling is already under way, at Tuleta and West Tuleta. G. D. H.

764.* April Completions Show Small Increase ; Fewer Drilling Wells. Anon. *Oil Gas J.*, 21.5.42, 41 (2), 11.—135 more wells were completed in April than in March, but the increase is partly due to working on a weekly basis and making April a five-week month. 20% of the completions were in the Appalachian district, which had 40% of the gas-wells. Ohio and Michigan showed considerable increases in activity, with Illinois and Indiana slightly ahead of March. Illinois completions were only 22% of the number for September 1941, and Oklahoma and Kansas had only 50% and 60% respectively of the activity at the corresponding time.

The numbers of completions in April and types are tabulated by States and districts, with the footage, and the numbers of wells in certain depth ranges. G. D. H.

765.* Location made in South Dakota for Test to Pre-Cambrian. Anon. *Oil Gas J.*, 21.5.42, 41 (2), 89.—Nearly 5,000,000 acres are reported to be under oil and gas lease

in South Dakota. The first deep test in Hughes County is to be drilled to the pre-Cambrian, which is estimated to be not more than 4500 ft. deep. It is on a 30,000-acre lease on a magnetic high. A test on the other side of the Missouri had oil showings in the younger formations. Tests drilled to the north and east found strong artesian flows in the Dakota and Sundance series. One found much gas in the Dakota. Little information has become available on three oil tests undertaken in South Dakota last year.

G. D. H.

766.* Illinois Production Trend may be Reversed. H. F. Simons. *Oil Gas J.*, 18.6.42, 41 (6), 16.—The Illinois daily production of oil in May was 281,000 bbl., compared with 287,000 bbl. in April, but it is felt that the downward trend may end after May, as has happened in previous years. The downward trend may be stopped by new discoveries or extensions, by multi-zone production technique, or by a well-planned deepening campaign.

During May there was evidence of an increase in wildcatting. In numerous cases there are possibilities of two-zone production, but not many pools seem favourable for deepening.

Secondary recovery programmes are becoming commoner in Illinois. Repressuring and water-flooding are being employed.

Tables show the new field discoveries and extensions in Illinois up to 9th June, 1942, with the location, depth, producing formation, initial production, and number of wells; the number of permits for wildcats and pool wells issued each month since October 1941; and the completions by pools and formations so far this year.

G. D. H.

767.* Kansas Wildcat Campaign Keeps Near Proven Areas. Anon. *Oil Gas J.*, 18.6.42, 41 (6), 66.—Fifteen new producing areas and new oil horizons have been discovered in Kansas during the first half of 1942. Only one discovery was over 3 ml. from a developed area. On the north-western extension of the Central Kansas Uplift no discoveries have been made north of the Ray pool. Wildcatting declined 50% in the first half of 1942 and the percentage of dry holes was doubled.

A gas discovery was made in Barber County, where two new oil-zones were found in old pools. A new Burbank sand-pool was found in Cowley County and a Mississippian pool in Marion County. The finds ranged from the Pennsylvanian to the Cambrian in age.

The Barber County gas discovery was in the Viola, but the well also showed oil saturation in the base of the Lansing, top of the Mississippian, Viola, and Simpson. A series of isolated developments are rapidly merging into a single stratigraphic trap accumulation on the south-east flank of the Central Kansas Uplift. Schweizer is the most northerly of five producing localities on the Peace Creek trend, and was discovered in February. The Smyres pool produces from the Mississippian chat. The Ray pool has been extended westward in the Reagan sand. At Lindsborg, which has also been extended, the Viola yields oil.

There are a series of north-east to south-west trends south of the Central Kansas Uplift, and a major trend parallel to the main high from Zenith north-west, and another parallel trend is developing from Cunningham at least into Pawnee County. However, many of the pools on the subsidiary trends were abandoned or had small quantities of gas and were not developed beyond the two-well stage.

A map shows the oil and gas discoveries in Kansas during the first half of 1942.

G. D. H.

768.* May Completions Hold Steady at Rate of 45 Daily. Anon. *Oil Gas J.*, 18.6.42, 41 (6), 84.—1421 wells were completed in U.S.A. in May, 846 being oil-wells. During May 1941 2669 wells were completed, 1879 being oil-wells and 554 dry. The indications of May 1942 are that wildcatting is still relatively near the 1941 level, but that the 40-acre spacing for oil-wells and the 160-acre spacing for gas-wells have greatly curtailed developmental drilling.

There were thirty-six more completions in Illinois in May than in April, and thirty-two less in Kansas. There was little change in the other States. The new Paluxy discovery in East Texas and the Tuscaloosa find in East Central Louisiana will probably increase wildcatting in those sectors.

The May operations are summarized by States and districts with the number of completions, oil, gas, or dry, the numbers in certain depth ranges, the footage drilled, and the number of wells drilling. G. D. H.

769.* Pressing Development Work in Alberta. Anon. *Oil Wkly*, 29.6.42, 106 (4), 46.—Areas not yet developed along the 20-mi. proven length of the Turner Valley oil-field are being intensively drilled. Efforts are being made to extend the field both north and south. In the northerly extension a well has been drilled into the upper and lower porous producing zones of the Madison. This well is on the east flank of the structure.

Outside Turner Valley the main contribution to increased production has been from Vermilion, where there are sixteen producing wells. G. D. H.

770.* Discoveries in Los Angeles Basin Fail to Maintain Reserves. L. P. Stockman. *Oil Gas J.*, 2.7.42, 41 (8), 54.—The Los Angeles Basin had produced 2,834,508,909 bbl. of oil up to the end of May 1942. All but a very small proportion of the production has been obtained from the Repetto (L. Plioc.) and the Puente (U. Mioc.), except at Long Beach, Inglewood, and Potrero, where the Pico (U. Plioc.) is productive. The basin has four structural trends parallel to the coast, and each trend has several fields. These trends are the Beverly-Newport line of shearing, the Playa del Rey-Wilmington trend, the Brea-Olinda-Montebello trend, and the Coyote Hills uplift. The Los Angeles Basin resembles the San Joaquin Valley in having many fields on the rim of the basin, accumulations following well-defined lines of folding and faulting, and general structural trends running north-west to south-east.

In the last ten years discoveries in the Los Angeles Basin have been few and far between, Wilmington being the only major discovery. Deep drilling revealed additional zones at Montebello and extended Dominguez westwards in 1939. In 1940 the Miocene Sentous zone was found to be highly productive at Inglewood, but the slow development has prevented its assuming importance. Turnbull Canyon, discovered in 1941, is only of secondary importance. The structure is a plunging, faulted nose cut off by a fault, with oil at about 3500 ft., probably from the Sycamore Canyon sand (U. Mioc.).

This year oil has been found at Buena Park at about 8900 ft. It is believed to be on a north-westerly-plunging nose, and may be from the equivalent of the Bell zone (Plioc.).

Unless a new line of folding is discovered it seems unlikely that many major discoveries will be made. Recently there has been a tendency to explore the rim of the basin, and in the east, where only relatively shallow drilling is necessary, previous work has shown heavy oil with doubtful commercial possibilities.

The area between El Segundo and Playa del Rey is to be tested, and deep sand production may be sought in the old Salt Lake field. Many believe that deep pays exist in the old Los Angeles City field. Only one well has been completed at Yorba Linda. This gave 766 bbl. of oil and 276,000 cu. ft. of gas/day from a depth of about 2300 ft. A deep test is being drilled at West Coyote.

The Los Angeles Basin fields are listed with the discovery date, number of producing wells, cumulative production up to the end of 1941, type of structure, depth, oil gravity, and average pay thickness. G. D. H.

771.* South Kansas Discoveries Open Shallow Pennsylvanian Trend. Anon. *Oil Gas J.*, 9.7.42, 41 (9), 56.—The discovery of Lansing-Kansas City lime production in the Lake City field proves a new trend running from Sun City in the north-west to Medicine Lodge in the south-east, a distance of some 20 mi. The new Pennsylvanian discovery at Lake City was in an old well plugged back from the Arbuckle. Sun City, 10 mi. to the north-west, also produces from the Pennsylvanian, the discovery well again having been plugged back from the Arbuckle.

The third Pennsylvanian sand discovery well on this new trend is $\frac{1}{2}$ mi. south of the Whelan Mississippian chat pool. This was completed in the Elgin sandstone with an initial potential of 3,900,000 cu. ft. of gas/day.

A table summarizes the geological data for the three Pennsylvanian discovery wells in northern Barber County, Kansas, and a map shows the positions of the wells. G. D. H.

Geophysics and Geochemistry.

772.* Resistivity Method of Locating Oil and Gas Pays. J. L. Harper. *Oil Gas J.*, 11.6.42, **41** (5), 64.—Electrical resistivity exploration has been carried out in and near oil-fields in various parts of the U.S.A. and Canada, the areas examined including rocks of most ages from Tertiary to the Cambrian. Both alternating and direct current were used, being supplied by a generator or batteries respectively. The best results were obtained with direct current.

The field procedure is briefly described, and a short account is given of the results of some of the investigations.

Under average field conditions 150–250 ft. in depth penetration can be done in an hour after the station is set up, and three to five stations can be occupied in a day. Depths of over 7800 ft. have been examined, and oil and gas can be located from the surface before drilling, the depth of the accumulation being indicated quite accurately. However, it is not known whether or not this can be done under all geological conditions.

G. D. H.

Polymerization and Alkylation.

773.* Economics of the Alkylation Process in the Production of High Octane Gasoline. R. G. Lovell. *Petrol. Engr*, March 1942, **13** (6), 27.—When planning the installation of an alkylation plant a survey of the availability of butylenes and isobutane in plant products must first be made. Consideration must then be given to the largest amount of butylenes which can be economically segregated for alkylation purposes, as this will determine the size of the plant to be installed. The surveying method is illustrated by considering hypothetical outputs and analyses of cracked gases, pressure distillate, and straight-run gasoline from a conventional refinery operating primary distillation and cracking plants and equipped with vapour-recovery systems. The availability of butylenes will depend on such plant factors as depth of cracking, vapour pressure of stabilized pressure distillate, blending agent employed, etc. The quantities of isobutane available from vapour-recovery systems, stabilization of the straight-run gasoline and of pressure distillate, should next be ascertained. If these quantities are insufficient to balance the butylenes available, the suggestion is made that a natural gasoline of 26–27 lb. Reid vapour pressure be obtained, stabilized in the plant to about 14 lb. vapour pressure, and the additional isobutane required extracted from the overhead product in a depropanizer-debutanizer unit. By taking a naphtha cut on primary distillation in addition to the gasoline and blending the mixture with the stabilized natural gasoline, an increase in the amount of straight-run gasoline base stock for premium-grade motor fuel could also be obtained. Flow diagrams of the various units are provided.

R. A. E.

774.* See Supply of Aviation Gasoline Enlarged Through Hydrofluoric Acid Alkylation. Anon. *Nat. Petrol. News*, 29.4.42, **34** (7), R. 131.—The new process is summarized as one in which isoparaffin hydrocarbons are alkylated with mono-olefinic hydrocarbons in the presence of liquid HF. It is claimed that propylenes, butylenes, and pentylenes may be alkylated either singly or together, thus making possible the use of very large quantities of cracked gases. The reaction takes place in the liquid phase, and since liquid HF boils at 20° C., temperature must be kept below 20° C. at atmospheric pressure. In the batch process described liquid isobutane and liquid HF are introduced separately into a line and mixed by charging through a pump, the butylene, or butylene and isobutane, then being admitted to the line. The mixture passes to a cooler, where the reactions proceed, and then to a settling tank. The hydrocarbons are fractionated, unconverted material being recovered overhead. Alkyl fluorides, produced as side reactions, are decomposed in contact with granular NaF or HF, the recovered hydrocarbon being recycled.

H. G.

775. Patents on Polymerization and Alkylation. Anglo-Iranian Oil Co. E.P. 546,037, 24.6.42. Appl. 23.12.40. In a process for the polymerization of olefins for the production of motor spirit a solid phosphoric acid catalyst is used, composed of orthophosphoric acid, copper orthophosphate, and calcium orthophosphate. The ratio

of orthophosphoric acid to the copper orthophosphate and calcium orthophosphate is higher than the ratio 4 : 1 : 1, but not substantially higher than the ratio 8 : 1 : 1.

H. Wolthan. U.S.P. 2,281,613, 5.5.42. Appl. 13.3.41.—Polymerization of a material selected from the group consisting of butadiene—1.3 hydrocarbons and mixtures of butadiene—1.3 hydrocarbons with copolymerizable compounds having a single C=C double linkage in aqueous emulsion in the presence of mercaptans having at least 6 carbon atoms in aliphatic linkage.

C. N. Kimberlin. U.S.P. 2,281,979, 5.5.42. Appl. 21.10.39. Process for the removal of over-polymerized constituents from polymerized oils by treating with a mixture of low-boiling petroleum hydrocarbons and a light oil boiling in the lubricating range.

K. Smeykal and K. R. Leuna. U.S.P. 2,282,499, 12.5.42. Appl. 1.9.38. Improved method of depolymerizing polymers of low-boiling olefins by passing them at an elevated temperature over a surface-active clay catalyst in which the clay itself is the effective catalytic component. Depolymerization is effected in the presence of an appreciable amount of steam, which operates on the clay itself to maintain the catalytic activity thereof.

H. B. M.

Drilling.

776.* **Drill Stem on Rotary Rig Cleaned with Steam.** Anon. *Petrol. Engr.*, June 1942, 13 (9), 44.—The pipe in the rat-hole is belled at the top and steam is connected to it. When the drill-stem is run into the rat-hole at the beginning of a trip out of the hole, or when waiting to set in another joint of drill-pipe, it is steam-cleaned as it is run in to remove drilling mud, old lubricant, etc. Part of the waste cleaned from the drill-stem and mud from the rotary hose drain down into the rat-hole pipe, and part drains off to the side beneath the rotary floor through a number of holes about 2 in. in diameter cut with a torch. When the rat-hole fills to the surface of the ground it overflows on to the ground through the 2-in. holes.

A. H. N.

Transport and Storage.

777.* **Reducing Internal Corrosion of Gasoline Pipe-Lines.** W. A. Schulze, L. C. Morris, and R. C. Alden. *Oil Gas J.*, 6.11.41, 40 (26), 172.—Although some 12,000 miles of gasoline pipe-line is in existence in the U.S.A., most is of recent construction, and only thirteen companies operate lines of more than 200 miles in length. Methods adopted by them for combating internal corrosion of the line are tabulated. Apart from procedure designed to reduce the quantities of air and water entrained and the use of scrapers, three methods utilized are: (a) removal of oxygen by means of sodium sulphite, (b) removal of water by dehydration of gasoline, (c) use of mercaptobenzothiazole (Rokon) dissolved in the gasoline as corrosion inhibitor.

One company previously using sodium sulphite has now discontinued the practice, and another, whilst still injecting, reports little tangible proof of the value of the addition. One company which reduces the moisture content of products pumped by 40/50% by means of bauxite has found the process beneficial, but it is pointed out that a disadvantage may arise due to introduction of water into the line during maintenance and retention of water in sections of line in hilly country.

The experiences of 2 years' operation with inhibitor added to gasoline at two pumping stations on a long line are recorded. Observations were made on test-bars weighing 500 gm. prepared from the same steel as the line, and inserted in the line at distances up to 100 miles from the injecting stations, and comparative observations were made on a section of the line more distant from the inlet end and where no inhibitor was injected. The results show very little corrosion of bars up to 100 miles from the injection point, but increasing with distance from that point in the case of inhibited gasoline. Bars in the uninhibited section showed rather severe corrosion. Losses in weight of bars after scale removal expressed as percentage per annum were nil from an inhibited section and 2–2.5 for uninhibited sections. Measurement of rust and scale from sediment traps on the intake side of pumping stations over a period of 6 months yielded comparable results, although differences in scraper usage and

flow rates may have contributed somewhat to differences in scale removal in various sections of the line. Examination of a small number of pipe-sections removed tends to confirm the value of the inhibitor, and so a third inhibiting station is shortly to be installed. Since the life-period of the inhibitor will vary with the type of gasoline pumped, careful control is necessary to decide the length of line which one station may protect. Intermittent injection may produce the desired effect, but further research on these problems is required. Another company using the process on a 50-mile section of 6-inch pipe-line found that it gave increased line capacity with reduced scraper usage, but that the cost of the inhibitor plus injection expenses did not justify its use. The economics of inhibitor usage are discussed. R. A. E.

778.* Method of Determining Pipe-Line Corrosivity Due to Soils. Paul F. Marx. *Petrol. Engr.*, Feb. 1942, **13** (5), 29.—The theories of a variety of authors are discussed and the principles of J. F. Putman are used to derive a fundamental equation connecting corrosivity with the specific resistance of the soil.

An instrument (of which a photograph is given, but which is not described) has been developed to establish the degree of corrosion and to predict pipe-life. Correlation of results given by the instrument and by U.S. Bureau of Standards pipe specimens shows that it should have practical use in construction and reclamation programmes.

A variety of data obtained with different soils, etc., are given in graphic form.

J. C.

779.* A Practical Application of Zinc Anode Protection to an 18-in. Pipe-Line. C. L. Brockschmidt. *Petrol. Engr.*, Feb. 1942, **13** (5), 74.—A detailed description, with many graphs, of a successful protective installation to a pipe-line in highly corrosive river-bottom land. Seven years after laying, the pipe-line began to spring leaks with increasing frequency and zinc anodes were finally installed.

Data obtained are given in the form of curves showing (a) soil-resistivity profile of terrain, with data bearing on the corrosion problem, (b) and (c) pipe/soil potential profiles for a series of six surveys made over a period of 830 days from the time zinc was connected, (d) current output of each cell of ten anodes, (e) and (g) zinc/soil potential, (f) open-circuit voltage zinc/pipe. Much of the data is also tabulated.

A few general suggestions are made for improvement in future installations.

J. C.

780. Practical Methods for Storing Volatile Liquids. D. E. Larson. *Nat. Petrol. News*, 1.4.42, **34** (13), R. 105.—The subject is discussed principally from the point of view of the minimizing of losses which are discussed under different headings. Sundry charts, which are reproduced, permit losses to be calculated and facilitate the choice of the most suitable type of storage. A means of assessing storage costs is also given. The classes of service to which the basic types of storage are best suited are: 1. Atmospheric tanks with fixed roofs and conservation valves for fuel oil, kerosine, low-volatility products. 2a. Breather roofs for gasoline in tanks that remain full or nearly full. 2b. Balloon roofs of large volume for gasolines in slow-working tanks. 3. Floating roofs for gasolines in tanks that work either continuously or intermittently. These roofs offer maximum fire protection. 4. Pressure tanks are the only practical means of storing natural gasoline and similar light products. 5. Underground storage is so expensive as to be justified only on the grounds of national security or because of city regulations.

H. G.

781.* Savings from Painting of Gasoline Storage Tanks. Anon. *Oil Gas J.*, 16.4.42, **40** (49), 51.—Tests conducted in the New York City area over an entire summer period on tanks filled with regular grade gasoline and having standard gooseneck connection showed the following losses expressed as percentage by weight: painted black, 9.2%; unpainted (average), 8.4%; painted aluminium, 7.28%; painted white, 5.60%; sunshaded, 5.18%. In the case of a 1000-brl. tank, it is estimated that the cost of labour and material for painting the whole tank white would be paid out in one and a half summers by the value of the gasoline saved, assuming the white paint has no effect on evaporation losses in winter months. Painting the roof only would be paid out in just over half a summer on a similar basis.

R. A. E.

Crude Petroleum.

782.* Viscosity of Crude-Oil Emulsions. Wm. Woelflin. *Oil Gas J.*, 19.3.42, **40** (45), 35.—Viscosity determinations were made mainly on brine-in-oil emulsions of both small and large particle size. The apparatus consisted of a reservoir with a paddle-stirrer from which a uniform mixture flowed to a funnel, the rate of flow being adjusted to keep the funnel constantly overflowing. The time of efflux of 100 ml. of sample was measured. Results were correlated with Saybolt Universal seconds by means of determinations with transformer oil, glycerine, and various crude oils, using the A.S.T.M. viscosity-temperature chart to convert observed viscosities to the same temperature. There is a straight-line relationship between Saybolt and funnel viscosity. Results are expressed in terms of "viscosity ratio"—i.e., the ratio of the viscosity of the emulsion at any temperature to the viscosity of the clean oil at the same temperature.

Using artificially made emulsions, the effects of particle size and of brine content were determined, and are shown by means of curves. The effect of particle size becomes of importance only at over 30% concentration. With increasing brine content viscosity gradually increases to about 40% brine, then abruptly to about 70–80%, at which stage there is generally a phase inversion to brine as the external phase and brine-in-oil emulsion as the internal phase, causing a drop in viscosity to just above that of 100% brine. Near inversion point the viscosity is very high, and the emulsion at this point, especially if the brine is finely divided, can be considered as a plastic solid. The conclusion of practical importance is that crudes should be pumped at low brine content or at extremely high brine content, although the latter case will involve pumping a very large volume of fluid.

A few experiments carried out on temperature effect showed the viscosity ratio for a given brine content to be independent of temperature. J. C.

Gas.

783. The Thermal Properties of a Wet Gas. G. G. Brown and F. Kurata. *Petrol. Engr.*, Dec. 1941, **13** (3), 23.—Enthalpy-entropy and temperature-entropy diagrams for wet gases, such as condensate, are presented, together with examples of the calculations necessary for their construction. The diagrams can be used for accurate calculations involving thermal properties—e.g., the computation of the drop in temperature accompanying a free expansion. J. C.

784.* Eliminating Hydrate Formation in S. Texas. F. H. Dotterweich. *Petrol. Engr.*, March 1942, **13** (6), 83.—Production of high-pressure natural gas in S. Texas producing areas is being accompanied by many problems relating to hydrate formation. The conditions existing, however, do not warrant the installation of dehumidifying plants in gathering lines, transmission systems or cycling plant operations. In most cases hydrate formation is induced only at infrequent short intervals, and heaters and heat interchangers are being employed. The work of Deaton and Frost is of great assistance in the design and operation of such equipment, and illustrations of the application of their data are given. In the removal of condensate in cycling plants three general methods are being used: (1) high-pressure oil absorption, (2) extreme cooling and separation with or without dehydration, (3) moderate cooling and separation. Application and operation of heaters and heat interchangers to permit satisfactory condensate removal and avoidance of hydrate formation are described. Insulation of the entire conditioning equipment to eliminate effects of variations in temperature and atmospheric conditions has been found to be of great value in a plant of the third type employing low-pressure oil absorption. The method employed in this plant for dealing with gases of varying character from different producing wells is also described. R. A. E.

Cracking.

785.* True Vapour Phase Process in Advanced Stage of Commercial Application. Anon. *World Petrol.*, 1941, Ann. Ref. Issue, **12** (11), 76.—In the T.V.P. process excessive gas formation is avoided by using as the heat medium for the vaporized

cracking stock a recirculated highly heated gas stream. A T.V.P. reforming unit recently constructed at Buffalo, N.Y., handles 1400 brl. of heavy and 800 brl. of light naphtha per diem, producing 91% of 401° F. E. Pt. gasoline of V.P. 9.3 lb. and O.N. 75-0. The addition of 1 c.c. of lead increases the O.N. to 82.5. The combined vapour-phase thermal cracking and pyrolysis of the recycle gas results in very complex reactions, including polymerization, isomerization, dehydrogenation, hydrogenation, and alkylation. The total cost of the plant is given as \$100 per barrel of heavy naphtha processed, so that the process would appeal to small refineries unable to afford the high investment costs of modern catalytic and reforming processes. An interesting potentiality of the process is the production of butadiene by increasing the reaction temperature and reducing the reaction time, treatment of a Pennsylvanian gas-oil giving 5.03% of butadiene out of a total yield of 14.94% of C.4 fraction. A 10,000-brl./day unit would thus produce approximately 25,000 tons per annum of butadiene. Aromatics may be produced at lower temperatures and longer reaction times, yields of 3.28% and 3.65% of toluene being obtained from E. Texas gas-oil and 200/400 Ill. naphtha, respectively. Details of yields from a semi-commercial unit are given, yields of up to 94.5% of gasoline being obtained, while the gases introduced show up to 50% conversion to gasoline.

A new T.V.P. cracking process has been worked out to operate on a reduced crude, but no operating date is at present available. C. L. G.

786.* Polyform and Gas Reversion Processes. E. R. Smoley and V. O. Bowles. *Oil Gas J.*, 6.11.41, 40 (26), 143.—In the U.S.A. approximately 100,000 brl. a day of naphthas, propane, and butane are processed in polyform and gas reversion plants, of which fourteen are in operation and four under construction. A.S.T.M. octane ratings of gasolines which can be produced with satisfactory yields from various charging stocks are: from straight-run heavy naphthas 76-80, from gas-oils of all types 74-76, from reduced crude 70-72, from heavy cracked gasoline 76. Inclusion of propanes and butanes from refinery or natural gas sources is advantageous in processing and provides additional quantities of high octane gasolines; about one-third of feed to existing plants consists of C_3 and C_4 fractions. The spread between A.S.T.M. and Research octane ratings of the gasolines produced ranges from 9 to 14 points. Aviation fuels meeting Army specifications and having an octane rating up to 91 with addition of less than 4 mls. T.E.L. per U.S. gal. can also be prepared. A description of the naphtha polyform process with provision for intake of C_3 and C_4 fractions is given, together with flow-sheet diagram. The application of the process to cracking of crude oil is illustrated by flow-sheet and described. The plant considered has a crude capacity of 22,000 brl. a day and replaces the conventional type of crude topping and cracking unit, a thermal polymerization unit, and a gas compression and absorption plant. Crude is charged via heat exchangers and a heater convection bank into an atmospheric topping tower, and straight-run gasoline is removed from the top. Heavy naphtha and kerosine side-streams are withdrawn through stripping-towers, and below the kerosine draw-off a straight-run gas-oil fraction is removed. This gas-oil with admixture with propanes and butanes is charged directly to the gas-oil polyform coil, where 34-45% of gasoline per pass is obtained. Heavy reduced crude from the bottom of the atmospheric tower is charged hot to the polyform viscosity-breaking coil after admixture with a side stream from the heavy tar stripper and propanes and butanes. Conversions per pass of 14-16% are obtained. Light recycle stock from the base of the fractionating tower is charged to the recycle coil with admixed propanes and butanes, yielding 25-32% gasoline per pass. The C_3 and C_4 fractions for these three coils are obtained from the stabilizer overhead, and consist of approximately 25% butanes, 75% propanes. Heavy naphtha passes over the absorber to remove C_3 and C_4 recycle from the residue gas and the enriched naphtha is charged to the naphtha coil. All four coils discharge to a common separator tower, the bottoms from which pass to the tar stripper, where fuel of the desired gravity is removed as bottoms; overhead fractions pass to the bubble-tower, and a side stream is removed for admixture with reduced crude prior to entering the viscosity-breaking coil.

The economics of butane and propane conversion in a naphtha polyform unit are discussed, and an example is given of a method for obtaining high yields of 100-octane aviation base and 73-octane motor fuel from casing-head gasoline of 26 lb. vapour pressure. This method involves separation of isopentane, *n*-butane, and isobutane,

followed by distillation to yield aviation base-stock and heavy naphtha. The heavy naphtha and *n*-butane would be charged to a polyform unit to produce motor gasoline and a butane/butylene fraction which would be charged to an alkylation plant, together with the *isobutane*, producing aviation alkylate and *n*-butane for recycle to the polyform plant. Blending of alkylate, *isopentane*, and aviation base-stock provides the 100-octane aviation base. Yield-octane relationships obtained from plant data when operating on 45-octane number mixed Texas naphtha with additional propanes and butanes are presented, and similar data provided for Californian naphtha of 58 octane number from pilot-plant operations. R. A. E.

787. Patents on Cracking. G. C. Connolly. U.S.P. 2,281,919, 5.5.42. Appl. 6.12.38. Method of cracking hydrocarbon oil to form lower-boiling hydrocarbons which involves contacting the oil at cracking temperature with a catalyst comprising a composite gel of silica and alumina containing up to 1% of an oxide of an element of group II taken from the class consisting of beryllium, magnesium, and cadmium.

K. M. Watson. U.S.P. 2,282,273, 5.5.42. Appl. 7.6.40.—Method of conversion of hydrocarbon oil by catalytically cracking a relatively light oil in the presence of a powdered cracking catalyst and under sufficient pressure to maintain a substantial portion in liquid phase. The vapours are separated from the catalyst, and one portion of the catalyst containing liquid reaction products is returned to the cracking operation. Another portion of the liquid reaction products substantially free from catalyst is subjected to pyrolytic conversion, together with a residual hydrocarbon oil. Cracked vapours are fractionated from this conversion process to separate reflux condensate from the fractionated vapours and at least part of the reflux condensate is passed to the catalytic cracking stage.

H. E. Drennan. U.S.P. 2,282,602, 12.5.42. Appl. 15.3.38. Method of conversion of low-molecular-weight olefins to hydrocarbons of higher-molecular-weight, which involves contacting the olefins with a catalyst comprising a moisture-free mixture of phosphorus pentoxide and a metal oxide selected from the group consisting of the oxides of copper, magnesium, iron, zinc, aluminium, tin, and nickel. The mixture is previously calcined under moisture-free conditions with a binder which produces a carbonaceous residue on heating.

G. Egloff. U.S.P. 2,282,855, 12.5.42. Appl. 29.6.40. Process for the conversion of hydrocarbons which involves heating a flowing stream of the oil to be cracked to a catalytic cracking temperature, while maintaining a dispersion of finely divided catalyst in the said stream. The resultant heated oil and dispersed catalyst is passed to one end of an elongated reaction zone, and the resultant conversion products are removed from the other end of the zone. A portion of the conversion products and catalyst are returned to the reaction zone, and from the remaining portion are separated cracked vapours and catalyst containing residue. The vapours are fractionated to form a reflux condensate, and afterwards to condensation to form distillate and uncondensed gases. The distillate is recovered, and regulated quantities of the uncondensed gases are returned to the reaction zone.

J. E. Ahlberg and C. L. Thomas. U.S.P. 2,282,922, 12.5.42. Appl. 20.3.37. Conversion of hydrocarbons by cracking hydrocarbons heavier than gasoline in the presence of an alumina-silica catalyst resulting from the co-precipitation of hydrated aluminium and silicon oxides in an aqueous menstruum containing ammonium hydroxide. H. B. M.

Refining and Refinery Plant.

788.* Solvent Refining Units at Ponca City Refinery. Anon. *World Petrol.*, 1941, Ann. Ref. Issue, 12 (11), 81.—Duo-sol, furfural, and methyl ethyl ketone units for the solvent refining of motor and industrial oils have been installed at a Ponca City, Oklahoma, refinery. These are integrated with the centrifuge dewaxing process used to dewax oils, which has been modernized to utilize hexane as the solvent, and also with the Bari-sol process. The Duo-sol plant handles 1600 brl. per day of heavy vacuum-distilled lubricating oil, and the furfural plant 1200 brl. per day of light wax distillate. The raffinate from the former is dewaxed in the hexane dewaxing

unit, and that from the latter in the methyl ethyl ketone plant. A 130° F. melting-point wax is produced from the M.E.K. crude scale wax. The Company's motor oil contains methyl dichlorostearate for greater film strength and thialkene to reduce oxidation tendencies.
C. L. G.

789.* Obtaining Asphalt Flux by Reducing Michigan Crude Oil. J. C. Albright. *Petrol. Engr.* Dec. 1941, **13** (3), 82.—A skimming plant, operated by the Producers Refining, Inc., to produce a variety of products, is briefly described. It utilizes a Michigan crude of mixed base, predominantly asphaltic, processing 2500 brl. daily. A variety of overhead and side streams are yielded, together with a residuum of 15° A.P.I., part of which goes to the vacuum reduction side of the refinery. The various conditions of operation—for example, temperature and degree of vacuum—to produce different products, such as S.C. 5 and S.C. 6, from the bottoms, are quoted. J. C.

790.* Blending to Improve Refinery Products. R. G. Lovell. *Petrol. Engr.* Feb. 1942, **13** (5), 41.—It is demonstrated how, after debutanization, the residual pentanes plus may have their vapour pressure raised to normal requirements by blending in *n*-butane, remaining from the de-*isobutanizing* operation. This, incidentally, will have a beneficial effect on the octane number. Curves are presented showing the amount of a natural gas component that can be substituted for another component without altering the vapour pressure.

Boiling ranges of blends can be predicted, less accurately, by an involved method of calculation, or by an easier graphical method.

It is shown how slight alterations in methods of plant operation may help to give bottoms of desired characteristics, when recovering *isobutane* and butylenes.

Other advantages of control of distillation range, etc., which are not indicated by the ordinary knock characteristics, have been demonstrated by the author by means of a car fitted with a variety of unusual instruments, enabling the following to be observed :—

Temperatures of :—

Gasoline in carburettor bowl.

Air to carburettor.

Gasoline-air mixture at carburettor discharge.

Gasoline-air mixture at front-centre-rear of intake manifold.

Exhaust gas from each cylinder.

Exhaust gas composite.

Barometric pressure.

Air saturation.

Intake manifold vacuum.

Power (relative in terms of equivalent grade).

Air-fuel ratio; each cylinder and composite.

Comparative, controlled tests with this mobile laboratory have shown that narrow distillation range and a low 90% figure and final boiling point gave a distinct improvement in performance, and it is considered that the better behaviour of the fuel in the engine is due to more complete atomization.

*iso*Pentane has an octane number of 89 and *n*-pentane of 69, so that substitution of *n*- by *iso*- would be advantageous. It is suggested that *isopentane* be added to butane and pentane-free stock to bring up the O.N., distillation range, vapour pressure, and gravity to such points that the specifications for 91 octane gasoline are met by adding the maximum amount of tetraethyl lead. Since *iso*- and *n*-pentane differ only little in vapour pressure and boiling point, separation would be difficult, requiring many trays, a high tower, and a high reflux ratio.

In general, response of hydrocarbons to tetraethyl lead depends on two factors: the base octane number and the chemical composition. The latter depends on the nature of the crude and the type of cracking practised with total sulphur content as the principal depressing factor in lead susceptibility. The sulphur compounds apparently react in the burning mixture to give lead sulphide, which is inactive as a knock suppressor. A chart is given showing the degree in which lead susceptibility is affected by the initial octane number of the base stock (assuming sulphur com-

pounds to be negligible). The effect of sulphur compounds is shown graphically from results obtained with a Californian straight-run, blends of this with heptene and blends of heptene with butyl mercaptan.

Some general inferences are made relating to the effects on the refining industry of the need for stock of high quality (other than cracked products) for aviation gasoline, and the consequent possibilities for the refiner. J. C.

791.* Complete Extraction of Liquefied Petroleum Gases. J. C. Albright. *Petrol. Engr*, Feb. 1942, **13** (5), 131.—A description, with a flow diagram, of a refrigerating or sub-cooling system, installed by the Cabot Carbon Co. at its Walton refinery, Texas, to obtain fuller extraction in the natural gasoline plant. Originally conventional practice was followed by absorbing the fractions from the rich gas by means of two absorbers in parallel, with the absorption oil and gas cooled to the lowest temperature practicable by ordinary atmospheric coolers—i.e., about 90° F. This temperature was not low enough for complete extraction of propane and butane necessary for the production of L.P.G. (liquefied petroleum gases). An additional absorbing column, built in two sections, has now been installed, to follow the two primary absorbers. Only the oil is chilled (to a temperature of 50° F.), the refrigerant being liquefied propane. There is a series flow of gas from the base to the overhead outlet, but an oil-collecting tray removes the oil from the lower part of the upper section to be withdrawn and passed through another propane chiller (the temperature again being reduced to 50° F.), from which it is immediately returned to the top of the lower half of the absorber. The unabsorbed gas from the top of the secondary absorber is used for fuel and carbon-black production, whilst the absorption oil from the base passes to a still. J. C.

792.* Influence of Alloy Additions on Corrosion Resistance. C. L. Clark. *Oil Gas J.*, 19.3.42, **40** (45), 48.—Results, obtained under specific operating conditions, for corrosion resistance of steels to hot petroleum products are presented graphically. They indicate that exactly comparable results may not be obtained from A.P.I. strip specimens and from commercial tubes, but that both types of test show that increasing chromium content imparts increasing corrosion resistance. Increased silicon content and the addition of aluminium seem to improve the resistance of actual tubes to a greater extent than in the case of the strip specimens. The character of the crude and variations in operating conditions may shift the various curves, but it is considered that the steels will retain their relative order of merit, and the curves should therefore serve as a useful guide in the selection of steels for refinery service. J. C.

793.* New Grapeland Plant Features Flexibility in Operation. W. C. Westbrook. *Oil Gas J.*, 16.4.42, **40** (49), 33.—A description is given of the construction and operation of one of the newest condensate-recovery and gas-cycling projects in Grapeland field, East Central Texas. Facilities are provided for processing up to 53 million cu. ft. of wet gas daily, and the plant at present handles the output from six producing wells, residue gas from the high-pressure absorber being injected into one injection well by compressors at a pressure of 2500 lb. Separate flow-lines from each well deliver gas to individual primary separators for initial separation of heavier condensate fractions, which re-enter the system with the rich oil-stream to the high-pressure re-absorber. After passing individual meters, the combined gases from the separators pass to three absorbers, the first being the high-pressure absorber operating at 1600 lb. pressure. The rich oil-stream from this absorber is combined with condensate from the primary separators and passed to a scrubber, where hydrates are trapped, and from thence to a high-pressure re-absorber operated at 400 lb. pressure. The low-pressure re-absorber operates at 70 lb. pressure, and the flash-vapours from the high-pressure re-absorber and vapours from the depropanizer feed-tank are recycled for re-absorption and fractionation. A centrifugal pump feeds lean oil to the low-pressure re-absorber and to the suction of a high-pressure pump, which feeds the high-pressure absorbers.

The still operates at 80 lb. pressure and has eight trays in the stripping section and twelve in the fractionating section. The depropanizer and debutanizer are described. The kerosine stripper takes its feed and reflux from the stripper

section of the still, and is built into one column with the lean oil reclaimer, which is an atmospheric fractionator, the feed and reflux of which come from the hot-oil circulating header at 480° F. Overhead vapours from the reclaimer are condensed, and pass to an oil-water separator. The oil level is maintained by a liquid-level controlled pump delivering to circulation or storage. Lean oil for heating the still, strippers, etc., is circulated to the oil-heater from a surge-tank equalized in pressure and temperature with the bottoms of the still. Plant fuel-gases are supplied by the light fractions flashed in the high-pressure re-absorber. Auxiliaries, control methods, and safety devices are described. Maximum daily production expected is about 65,000 gal. motor fuel, 25,000 gal. butane, 2500 gal. kerosine, and 500 gal. fuel oil.

R. A. E.

794. The Performance of Refinery Gas Absorbers with and without Intercoolers. R. M. Jackson and T. K. Sherwood. *Nat. Petrol. News*, 29.4.42, **34** (17), R. 134.—Data, relative to full-scale refinery operations, are given for the operation of an absorber working on mixed gases. It is shown that the use of intercoolers increases recovery, the advantage gained being greater in the winter than in the summer, owing to the lower temperatures prevailing in the winter. The work afforded opportunity of comparing observed data with the results of standard calculation. It was concluded that, with the exception of calculations involving methane, agreement was good.

H. G.

795. Patents on Refining and Refinery Plant. U. B. Bray. U.S.P. 2,281,667, 5.5.42. Appl. 22.7.33. Method of refining petroleum oil which includes mixing the oil with liquefied hydrocarbon gases having a vapour pressure greater than atmospheric, cooling the mixture to a temperature sufficient to congeal the wax content, passing the cooled mixture through a settling tank, and afterwards separating from it the remaining portion of wax by filtration.

V. L. Chechot. U.S.P. 2,282,033, 5.5.42. Appl. 3.11.39. Process of refining viscous hydrocarbon oil which involves adding to it a small quantity of finely divided mica and talc and afterwards separating from the treated oil the mica-talc mixture containing entrained acid-sludge.

W. J. Mattox. U.S.P. 2,282,231, 5.5.42. Appl. 19.4.41. Method of separating ethyl benzene from a mixture containing essentially ethyl benzene and isomeric xylenes. The mixture is fractionally distilled to remove a relatively lower boiling fraction containing *m*- and *p*-xylenes and ethyl benzene from a residue of higher-boiling *o*-xylene. The relatively lower-boiling fraction is subject to catalytic hydrogenation to form a naphthenic hydrocarbon mixture, including *cyclohexane* and dimethyl *cyclohexanes*. The mixture is then separated by distillation into dimethyl *cyclohexanes* and an ethyl *cyclohexane* fraction, and the latter catalytically dehydrogenated to give ethyl benzene.

M. A. Dietrich. U.S.P. 2,282,710, 12.5.42. Appl. 14.6.39. Method of inhibiting the deterioration of hydrocarbons in the presence of metals normally active to catalyse deterioration. Incorporated in the petroleum hydrocarbons is a small amount of an organic compound having an amino nitrogen atom and a divalent sulphur atom, each singly bonded to adjacent aliphatic carbon atoms in open-chain configuration. The second valence of the sulphur atom is satisfied by a member of the group consisting of hydrogen and aliphatic radicals.

L. U. Franklin and W. H. Weeks. U.S.P. 2,284,273, 26.5.42. Appl. 20.7.39. Method of sweetening sour petroleum oils containing mercaptans by suspending in a flowing stream of the oil, in the presence of an oxygen-containing gas, a substantially dry solid mixture of asbestos, and a substance capable of reacting with the mercaptans to form sweet sulphur compounds, and of regeneration by the oxygen-containing gas.

W. H. Rupp and K. E. Thorp. U.S.P. 2,284,592, 26.5.42. Appl. 23.3.40. Process for the recovery and segregation of hydrocarbons containing three carbon atoms in the molecule and fractions containing four carbon atoms in the molecule derived from the cracking of petroleum oils.

C. D. Marshall. U.S.P. 2,284,607, 26.5.42. Appl. 3.10.41. Method of dewaxing a waxy petroleum oil-stock by admixing with it a solvent in amount to maintain the mixture fluid at temperatures near, but somewhat above, final dewaxing temperature. Then a second portion of solvent is added, and the mixture so formed finally chilled to dewaxing temperature and the wax separated therefrom.

H. B. M.

Metering.

796.* Dew-Point Recorder Utilizing Photo-Electric Relay Safeguards Gas Line Against Freezing. J. A. Setter. *Petrol. Engr*, Feb. 1942, 13 (5), 134.—A description, with a schematic diagram, of a novel dew-point recorder utilizing a General Electric photo-electric relay. Continuous readings are given of temperature at which condensation occurs when natural gas enters the Denver metering plant of the Colorado Interstate Gas Co. The gas passes through a gold-plated U-tube, immersed in a freezing solution, fitted with plate-glass windows, above which are mounted a General Electric light source and photo-electric relay. When the gas is chilled a film of condensate is deposited on the inside of the U-tube, reducing reflection to the photo-tube, which operates to disconnect the cooling coils and connect heaters to warm the solution. The process repeats when the condensate disappears, and a recording-bulb-type thermometer records the temperature of the solution, giving a curve similar to a sine wave. The gas pressure is also recorded on the same chart, and from the two records the dew-point is calculated.

J. C.

Chemistry of Physics and Hydrocarbons.

797. Heats of Isomerization of the Nine Heptanes. E. J. R. Prosen and F. D. Rossini. *Bur. Stand. J. Res.*, Wash., 1941, 27 (6), 519-528.—Calorimetric measurements have been made which yield values for the differences in the heats of combustion of all the nine heptanes except 2-methylhexane and 3-methylhexane for the liquid state at 25° C. Values for these two in reference to *n*-heptane were determined from the corresponding values for the differences in the heats of combustion of *n*-hexane, 2-methylpentane, and 3-methylpentane, and of *n*-octane, 2-methylheptane and 3-methylheptane. These values for the differences in the heats of combustion which are also the heats of isomerization in the liquid state at 25° C. have been combined with calculated values for the differences in the heats of vaporization to give values for the heats of isomerization in the gaseous state at 25° C.

A description of the preparation of the heptanes is given. The calorimetric procedure was the same as that in the work on hexanes previously reported. The following values were obtained:

Isomer.	Heat of isomerization ΔH for $nC_7H_{16} = iC_7H_{16}$.		
	Liquid.	Gas.	
	25° C. k.-cal./mole.	25° C. k.-cal./mole.	0° K. k.-cal./mole.
<i>n</i> -Heptane	—	—	—
2-Methylhexane	-1.30 ± 0.25	-1.80 ± 0.29	-1.21 ± 0.31
3-Methylhexane	-0.72 ± 0.25	-1.18 ± 0.29	-0.42 ± 0.31
3-Ethylpentane	-0.14 ± 0.23	-0.52 ± 0.27	+0.48 ± 0.30
2:2-Dimethylpentane	-3.42 ± 0.28	-4.45 ± 0.32	-3.40 ± 0.34
2:3-	-2.18 ± 0.26	-2.80 ± 0.30	-1.71 ± 0.32
2:4-	-2.54 ± 0.16	-3.40 ± 0.22	-2.32 ± 0.25
3:3-	-2.44 ± 0.15	-3.24 ± 0.21	-2.23 ± 0.24
2:2:3-Trimethylbutane	-3.00 ± 0.22	-4.17 ± 0.27	-3.02 ± 0.30

D. L. S.

798. Free Energies and Equilibria of Isomerization of the Butanes, Pentanes, Hexanes, and Heptanes. F. D. Rossini, E. J. R. Prosen, and K. S. Pitzer. *Bur. Stand. J. Res., Wash.*, 1941, **27** (6), 529-541.—Values are reported for: (a) the standard-free energy of isomerization divided by the absolute temperature $\frac{\Delta F^\circ}{T}$, (b) the relative

amounts of the several isomers present when at equilibrium with each other for the two butanes, three pentanes, the five hexanes, and the nine heptanes, all in the ideal gaseous state for the range 298-1000° K. The results are presented both in tabular and graphical form. Comparison is made of these calculated values of the equilibrium concentrations with the directly measured values reported by other investigators for equilibria involving the two butanes, two pentanes, and four hexanes.

It is concluded that at 298° K. the normal isomer is thermodynamically the least stable in each case, with the exception that 3-ethylpentane is less stable than *n*-heptane. Relative to the other isomers, the normal isomer increases in stability with increase in temperature, and at 1000° K. is among the most stable of the isomers.

At 298° K. the 2 : 2-dimethyl isomer is in each case the most stable, but it rapidly becomes less stable with increasing temperature, and at 1000° K. is among the least stable of the isomers.

D. L. S.

799. The Alkyl Nitrates. Anon. *Chem. Tr. J.*, 9.1.42, **110**, 35.—Sharples Solvent Corporation in E.P. 540,150 of 1940 describe an improved method for production of alkyl nitrates, particularly applicable to manufacture of propyl and amyl nitrates. The process comprises treatment of an aliphatic alcohol with nitric acid of 35-68% concentration, removing the nitrate by azeotropic distillation under a reduced pressure, and returning or adding to the reaction mixture that component of the reaction products which is in excess of the equimolecular proportion in the distillate, so as to remove both products of reaction in equimolecular proportions and to prevent an accumulation thereof in the reaction mixture. Auto-oxidation in the esterification vessel is prevented by removing the alkyl nitrate from the vessel promptly after formation. Urea solution is also added periodically in quantities sufficient to inhibit oxidation.

R. A. E.

800. Chlorinated Olefins. *Chem. Tr. J.*, 20.2.42, **110**, 207.—E.P. 542,086 of 1941 issued to Shell Development Co. of California describes a method for halogenation via substitution of unsaturated aliphatic hydrocarbons with the aid of a catalyst at temperatures about 300-310° C. in the presence of less than 2-3% oxygen.

R. A. E.

Analysis and Testing.

801.* Test Methods for Control of Gasoline Treating Processes. A. W. Trusty. *Petrol. Engr*, Jan. 1942, **13** (4), 58.—The effect of excess sulphur and polysulphides on the lead susceptibility and gum-inhibitor requirements of gasoline has emphasized the necessity of proper treating. Several easy methods of testing stock, developed as aids to the refiner, are described. These comprise:—

(1) Hydrogen sulphide in raw stock by reaction with acidified cadmium chloride solution.

(2) Mercaptan content of sour stock, by two methods:—

(a) The "copper number" test: addition of ammoniacal cupric sulphate to the H₂S-free stock until the blue colour persists.

(b) Addition of excess silver nitrate solution and back titration with ammonium thiocyanate.

A knowledge of mercaptan content is valuable in copper chloride treating, in caustic washing, and in doctor treatment. In the latter treatment it acts as an index of the correct quantity of free sulphur for making the "break."

(3) Litharge in Doctor Solution by acidification with acetic acid and titration with ammonium molybdate, using tannic acid as indicator.

(4) Butyl-mercaptan test. Addition of this reagent gives an orange or brown precipitate if the gasoline contains corrosive sulphur.

(5) Peroxides in gasoline by means of thiocyanate.

In addition, methods are described for the analysis of caustic soda containing sodium sulphide and mercaptides, using potassium iodide-iodate reagent. J. C.

802. Fluorescence Analysis Reaches Practical Development Stage. F. B. Taylor. *Oil Wkly*, 22.6.42, 106 (3), 27.—The fluorescence shown by oil has been used to detect oil in mud streams, in cores, old and new, and in the examination of lubricants and lighter stocks.

Ultra-violet rays striking an atom may drive an electron into a new orbit, and the return of the electron to its former orbit may give out energy in the form of light. Not all atoms can give rise to fluorescence, and certain wave-lengths of ultra-violet light are needed to cause fluorescence in those substances capable of giving it.

Several sources of ultra-violet rays are available. Observations of fluorescence must be made in the dark.

Experience is necessary to interpret the meaning of differences in the fluorescent colours. It may be necessary to dissolve the oil in a solvent in order to observe the fluorescence. In some respects the method is over-sensitive, and therefore all indications must be interpreted according to the circumstances. Thus cores too tight to give commercial production may give brilliant fluorescence.

Substances other than oil may give fluorescence.

G. D. H.

Motor Fuels.

803.* Sulphur Limits in Gasoline. Lowry and Egloff. *Oil Gas J.*, 11.12.41, 40 (31), 52.—A reasoned plea is made for the relaxation of sulphur restrictions in gasoline, and is backed by reference to many well-known authorities.

In parts of U.S.A. there is still in operation a sulphur maximum of 0.1% for gasoline. This low limit was derived arbitrarily at a time when the sweet, relatively sulphur-free crudes of the East and Mid-continent were abundant and were the main sources of motor fuel. The newer, cracked spirits from Texas, California, etc., caused antipathy because they differed in colour, odour, gravity, and sulphur content, but in all respects except sulphur the prejudice has been overcome. Strong evidence is presented that only free sulphur and mercaptans are harmful, and these are invariably removed by careful refiners. Other sulphur compounds, such as thiophenes, are harmless. Actual corrosion in motor-car engines is shown to be due mainly to water condensation, and in present-day cars is prevented by control of jacket-water temperature and ventilation of the crankcase. A wide variety of examples of the use of high-sulphur-content gasolines, without deleterious effects, are quoted, including an abnormal example of a mixture containing 5% carbon disulphide, which caused no damage. Further arguments are based on diesel-fuel specifications, and perhaps the authors' strongest point is the fact that high-sulphur-content spirits have been used on the West Coast for 15 years, in all kinds of climates, without causing any unusual wear.

It is necessary to raise these unjustifiably low sulphur limits to prevent wastage of natural resources through excessive refining of motor fuel.

J. C.

804. New Specifications Issued by British Petroleum Mission. Anon. *Nat. Petrol. News*, 24.12.41, 33 (52), R. 408-R. 410, R. 416—Revised specifications for twenty-one products, including four new ones, have been issued by the British Petroleum Mission in Washington governing requirements of the British Government under lease-lend arrangements. The four additions concern finished alkylate for blending into 100-octane aviation gasoline, low-cold test distillate or residuum for lubes, Columbian lube distillate, sodium-naphtha-sulphonate (soluble cutting-oil base). The specifications are given in full, together with a list of the official test methods. The following specifications are unchanged: pool motor gasoline, white spirit, gas oil, diesel oil, marine diesel, marine fuel, W/D gas oil, special refinery gas oil, and Admiralty fuel oil.

H. G.

805. Indian Power Alcohol. Anon. *Chem. Tr. J.*, 30.1.42, 110 (2854), 125.—Increased attention is being paid to the use of power alcohol from molasses as a blending

agent to conserve motor-spirit supplies. Schemes operating or under consideration aim at including up to 20% of alcohol. Admixture of alcohol has been compulsory in Mysore State since October 1939, and in United Provinces since 1940. Similar schemes are planned for Bombay. Much of the molasses from the 150 or more sugar factories in India is at present wasted. An expert committee appointed by the United Provinces and Behar estimated alcohol production costs to be less than 6½ annas (8d.) a gallon if molasses cost 6 annas a maund (82 lb.) at distillery. With a normal annual consumption of motor spirit of about 100 million gal., admixture of 20% alcohol is of considerable national advantage. R. A. E.

806. British Specifications Revised for Aviation Fuel Base Stocks. Anon. *Nat. Petrol. News*, 1.4.42, **34** (13), R. 102.—The revised or modified specifications for petroleum products agreed with the British Petroleum Mission in Washington are given. Revisions occur in the specifications for the unleaded base-stocks of 100, 91, and 87 O.N. aviation fuel, special refinery gas oil, pool light and heavy fuel oil, The specifications for hydraulic and transformer oil are modified. H. G.

807. Patents on Motor Fuel. R. B. Day and E. R. Kanhofer. U.S.P. 2,283,851, 19.5.42. Appl. 31.3.41. Process for the production of gasoline by subjecting a combined feed to catalytic cracking, fractionating from the products of this operation, gasoline, light intermediate conversion products, and heavy intermediate conversion products. The heavy intermediate conversion products are mixed with light intermediate conversion products formed in a thermal cracking process, and the mixture is subjected to thermal cracking to form substantial quantities of gasoline.

B. S. Friedman and W. L. Benedict. U.S.P. 2,283,854, 19.5.42. Appl. 5.7.40. Production of a substantially saturated gasoline of high octane number by cracking a hydrocarbon oil in the presence of a powdered cracking catalyst and of a hydrogen-containing gas. Conversion products are separated into a hydrogen-containing gas, a gasoline fraction containing substantial amounts of unsaturated hydrocarbons, and a higher-boiling fraction. Part of the higher-boiling fraction is returned to the cracking operation. The gasoline fraction is combined with a hydrogen-containing gas and a naphthenic oil, and the mixture is subjected to contact with a dehydrogenating catalyst to form a substantially saturated gasoline. H. B. M.

Lubricants and Lubrication.

808.* Recovery of Used Lubricating Oils. V. Biske. *Petroleum*, Nov. 1941, **4** (7), 147.—It is considered that the bulk of used oil available for recovery will be that used in internal-combustion engines, turbines, transformers, and other electrical equipment. Types of contaminants present in these oils, their origin, and effects are briefly reviewed. Purifying methods involving settling or filtration are of value in prolonging the useful life of oils, but eventually the oil must be discarded on account of increasing content of contaminants of the soluble type.

At present numerous relatively small plants using a variety of processes, and limited in scope both as regards the type of oil which can be treated and the degree of restoration of quality, are engaged in the recovery of used oil. Treating losses and running costs are also greater for these relatively small plants as compared with those of large plants. It is therefore considered that recovery of used oils could be achieved more efficiently in petroleum refineries, with greater flexibility in respect of feed-stock and production of finished products. Careful segregation of the various types of used oil is expensive and complicated, and it is suggested that the more centralized distribution and use of fresh oils applying under present conditions would enable returning tank-cars or returnable drums to be used for the delivery of used oils to the refineries. Flushing oil used for cleaning tank-cars so used could be added to the material to be recovered. Exclusion only of compounded and black oils is considered necessary.

Broadly speaking, normal refining procedure could be adopted, involving distillation to remove diluent and separation of spindle and medium lubricating-oil distillates, leaving a residue of long residuum type. The diluent separated might be used for

diluting oils received in order to accelerate separation of insolubles and render the oil more easily pumpable, or used as cracking stock or for fuel purposes. The lubricating distillates could be refined by acid or solvent extraction as desired. Treatment of the residue may be difficult on account of the presence of asphaltic material, and if considerable quantities of additives or grease are present, refining may not be an economic proposition. It is realized that the scheme may involve degrading some of the high-grade components, and that production of certain special types of oil normally obtained from selected crudes would be impossible from the mixed used oils. Nevertheless, the oils so produced would command a considerable market. Other advantages of a centralized scheme are enumerated. R. A. E.

809.* Lubrication without Oil. A. H. Stuart. *Petroleum*, Jan. 1942, 5 (1), 9.—Efficient lubrication of steam-engine cylinders has been maintained by the use of a dispersion of colloidal graphite in water, the graphite producing an anti-friction surface on the cylinder walls and showing no sign of being carried over by the exhaust steam.

In the lubrication of bearings made of cotton fabric bonded by synthetic resin, addition of colloidal graphite to water reduces the coefficient of friction under conditions of high load or high speed. Good results have also been achieved by soaking the cotton fabric in a dispersion of colloidal graphite in water or other suitable medium before bonding with the resin. Curves relating maximum load to variation in speed under conditions of at least 5 hours' running without seizure under dry conditions show the improvement obtained by this treatment of the cotton fabric. With plain-water lubrication it is estimated that the seizing load is increased by 35% if the cotton fabric is first impregnated with colloidal graphite, and nearly doubled if colloidal graphite is also incorporated with the lubricating water. R. A. E.

810.* Engine Bearing Temperatures (Road Tests).—I.A.E. Research Committee Report. J. Spiers. *J. Instrn. Auto. Engrs*, 1942, 10 (6), 129–156.—This report deals with tests on a 10-h.p. car, the engine of which was equipped with eighteen thermocouples in the sump, oilways, and bearings. In general, the results confirmed previous bench tests; the factors mainly influencing bearing temperatures are as follows, in order of importance :—

1. *Engine Speed.* Bearing and oil temperatures increase either linearly or at an increasing rate with increasing speed, and are substantially independent of load.

2. *Viscosity.* A change from S.A.E. 50 to S.A.E. 10 oil reduced the big-end bearing temperature from about 77° C. to 65° C. at 2000 r.p.m. and from 138° C. to 90° C. at 4000 r.p.m.

3. *Oil Temperature.* Reduction in oil sump temperature is reflected to a greater or less extent in bearing temperatures.

4. *Air Temperature.* 83–85% of any air temperature variation is reproduced at the engine bearings.

5. *Water Temperature.* Not more than 25% of any change in jacket temperature is reflected in bearing temperatures.

6. *Oil Pressure.* Increase of pressure, and consequently of flow, results in a small reduction in bearing temperatures. K. A.

811. Patents on Lubricants and Lubrication. C. F. Prutton. U.S.P. 2,281,597, 5.5.42. Appl. 25.6.37. Preparation of a lubricant consisting of a major proportion of a lubricating oil and up to 20% of a halogenated alkylated aromatic ketone.

D. R. Merrill. U.S.P. 2,281,705, 5.5.42. Appl. 3.1.40. Extreme pressure lubricant consisting of mineral lubricating oil and a small percentage of chlorinated Edeleanu extract.

U. B. Bray. U.S.P. 2,281,824, 5.5.42. Appl. 22.9.39. Manufacture of a lubricating oil containing a relatively small proportion of an alkaline-earth metal soap of a saponifiable organic acid to overcome the deposit of resinous and varnish-like materials in severe service internal-combustion engines. Additionally there is incorporated a small quantity of an oil-soluble alkaline-earth metal compound of a

thio-phenolic derivative to overcome corrosion conditions developed in the oil. The added constituents do not materially increase the viscosity of the original oil.

G. H. Von Fuchs and H. Diamond. U.S.P. 2,281,894, 5.5.42. Appl. 18.1.40. Preparation of a lubricating or electrical oil composition consisting of a highly refined mineral lubricating oil and dissolved therein a small amount of a highly cracked distillate oil, free from tar and selected from the group consisting of coking cycle stock and cracking coke blow-down oil. The composition is claimed to have greater resistance to oxidation than mineral oil.

C. F. Prutton. U.S.P. 2,282,343, 12.5.42. Appl. 1.3.39. Manufacture of a lubricant consisting of 80% mineral lubricating oil and 0-1-20% of both an oil-soluble, halogen-bearing, oxygen-free organic compound and an oil-soluble, organic oxygen compound.

E. W. Cook. U.S.P. 2,282,707, 12.5.42. Appl. 10.12.38. Lubrication of bearing surfaces at least one of which comprises an alloy having substantially the corrosion-susceptibility of cadmium-silver, cadmium-nickel, and copper-lead alloys. The lubricant has incorporated in it corrosion-inhibiting proportions of an oil-soluble organic metallic sulphide.

F. W. Downing and C. J. Pedersen. U.S.P. 2,282,513, 12.5.42. Appl. 19.5.39. Incorporation into a viscous petroleum oil normally subject to deterioration in colour of a small amount of an organic compound of the type of a Schiff's base, obtained by condensation of 1 mol. of an aliphatic polyamine containing at least two primary amino-groups directly attached to different carbon atoms of the same open chain with at least 2 mols. of an aldehyde, so that one and only one mol. of aldehyde reacts for each primary amino group of the polyamine.

S. R. Scalzitti. U.S.P. 2,283,581, 19.5.42. Appl. 22.1.40. Preparation of a lubricant consisting of 94% of an oily base, 3% of zinc sulphide well dispersed therein, 3% of barium sulphate for retarding decomposition of the zinc sulphide by overheating between movable parts of machinery.

B. T. Brooks. U.S.P. 2,284,258, 26.5.42. Appl. 6.1.40. Preparation of a lubricating composition consisting of a mineral lubricant and a small amount of an oleone.

H. B. M.

Asphalt and Bitumen.

812. **Patents on Asphalt and Bitumen.** E. Thelen. U.S.P. 2,281,728, 5.5.42. Appl. 9.3.39. Method of treating a charging stock of asphaltic crude and residue which involves first heating the charging stock to approximately 270° F. and then adding 0.4-1.2% of 22 Baumé hydrochloric acid. This is done under conditions designed to effect substantially complete absorption of free hydrochloric acid. Finally the mixture is air-blown at 425° F.

R. E. Burk. U.S.P. 2,282,703, 12.5.42. Appl. 28.10.36. Process for making asphalt which involves oxidizing petroleum residuum by heating and agitating in exposure to oxygen and thickening the material to the desired melting point and penetration. After oxidation there is incorporated a small amount of a naphthenate of a metal of the group consisting of cobalt, manganese, iron, lead, vanadium, and zinc.

H. B. M.

Special Products.

813. **Patents on Special Products.** W. J. Backoff, N. D. Williams, J. F. O'Loughlin, H. L. Moir, and J. S. Yule. U.S.P. 2,284,080, 26.5.42. Appl. 6.10.38. Preparation for use as a gum solvent and consisting of 50-90% of refined mineral oil boiling above the boiling range of kerosene and 50-10% of a mixture of esters of phthalic and benzoic acids, the esters boiling above 350° F.

H. B. M.

Coal and Shale.

814. Swedish Shale Oil. Anon. *Chem. Tr. J.*, 30.1.42, 110 (2854), 132.—A new method for shale-oil extraction being developed by the Svenska Skifferoljeaktiebolaget, and due to Dr. Ljungström, consists fundamentally of heating the shale *in situ*, and experiments are said to have given promising results. The shale-beds in Närke are estimated to be sufficient for production of about 100 million tons of oil, but as the oil content even in the richest beds is not more than about 6%, production costs in peace-time were too high to enable competition with imported liquid fuel. By the method proposed, a number of vertical bore-holes are made in the deposit; in some, electrical heating elements are installed, whilst others are used to convey oil vapours and gas into condensers at ground level. The average depth of the shale deposit is 17–18 metres. By suitable arrangement of heaters it is estimated that the quantity of shale heated in each boring would be 400 tons, the heating period $2\frac{1}{2}$ months, and power consumption 40,000 kw.

To produce 30,000 tons of oil per annum would require 2700 electrically heated borings and the heating of 1 million tons of shale.

R. A. E.



INSTITUTE NOTES.

SEPTEMBER, 1942.

FORTHCOMING MEETINGS.

The next meeting will take place on October 20th at the Junior Institute of Engineers.

CANDIDATES FOR ADMISSION.

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

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

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

ANDERSON, Ronald Turnbull, Asst. Works Chemist, The Shell Company of Australia. (*T. Hartigan ; H. W. Stevenson.*)

CURRAN, Bernard Reginald, Manager, Industrial Traders, Ltd. (*Harold Moore ; H. E. Charlton.*)

HURRELL, William Mark, Manager, Installations Branch, Distribution Department, Anglo-Iranian Oil Co., Ltd. (*Dr. A. E. Dunstan ; G. H. Coxon.*)

MACNEILL, Ian Victor Noble, Assistant Operating Superintendent, Magnesium Metal Corporation. (*J. E. Hackwood.*)

SCHNABEL, Dr. Fred, Chemical Engineer. (*L. Ivanovszky ; V. Biske.*)

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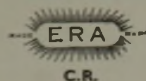
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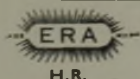
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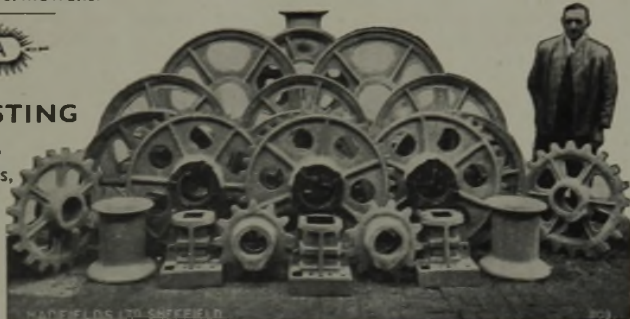
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
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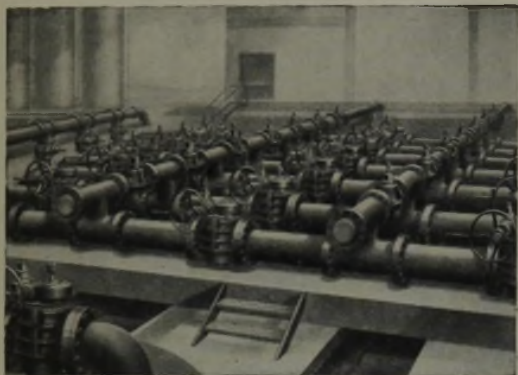
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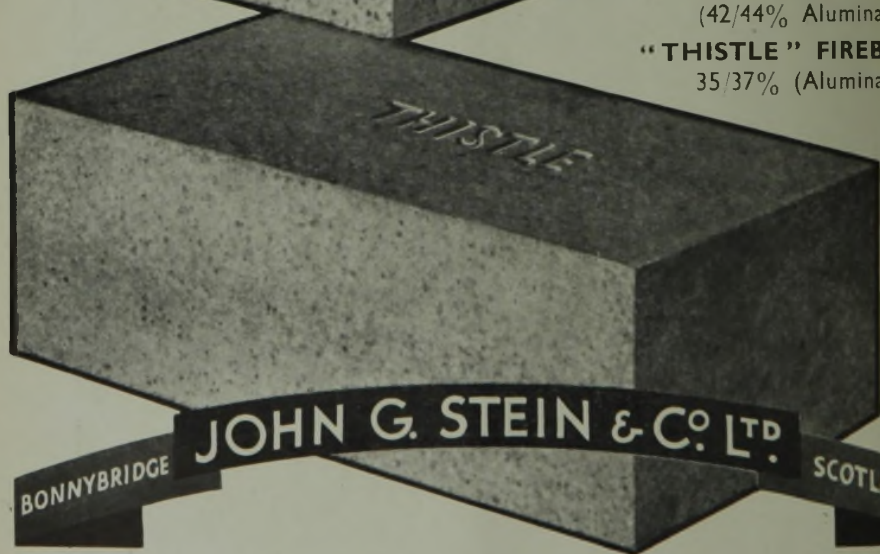
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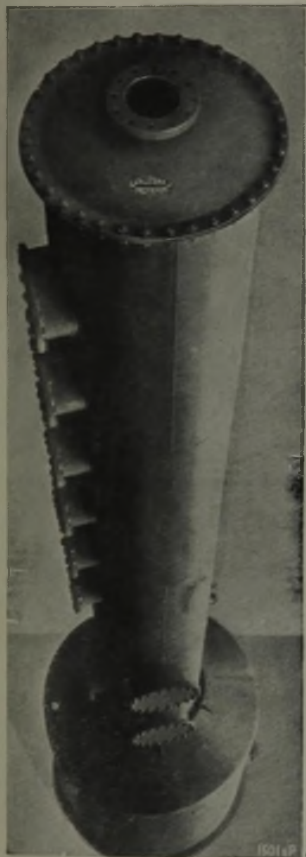
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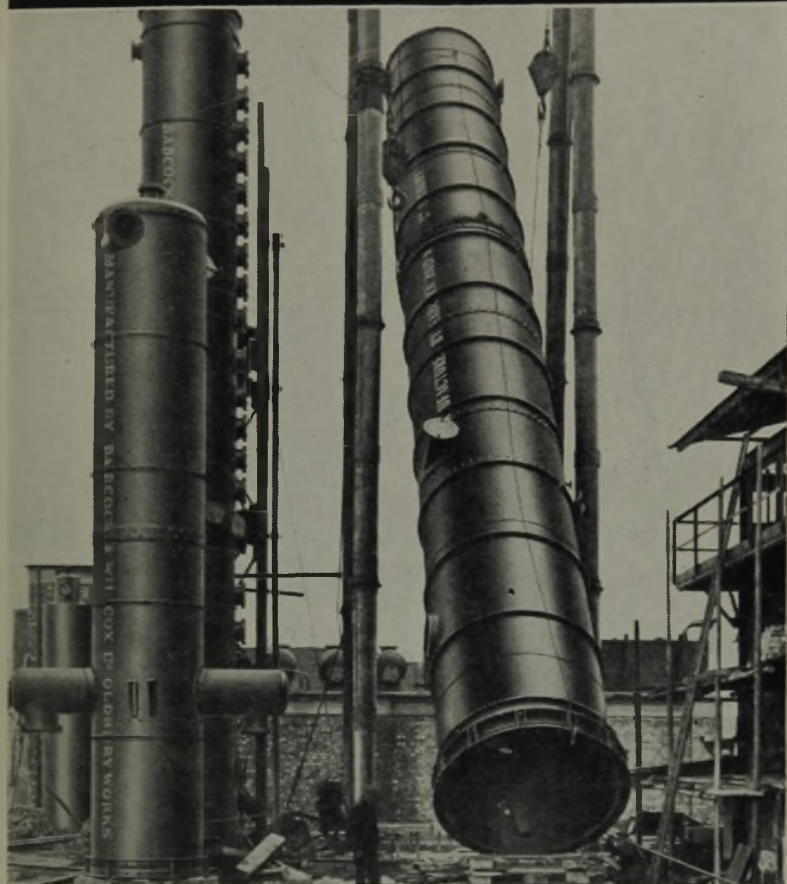
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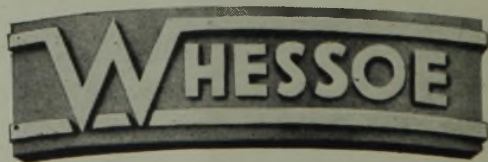
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