# THE SEPARATION OF THE COMPONENTS OF PETROLEUM.

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A THESIS

by

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# PREFACE.

It is the author's desire to express his deep gratitude to Professor Thomas Gray of the Royal Technical College, Glasgow, for the kind interest he has shown in this work. He has been throughout, not only a supervisor but a friend, ready at all times to offer stimulating suggestions and steadying criticisms, both of which were always of such nature as to encourage and to inspire.

P. F. G.

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others, it must be admitted, might most profitably be used as fuel and for lubrication. Even if for the latter purposes however, hydrocarbons of known chemical composition and physical structure could be more beneficially utilised. From a purely chemical point of view the study of the structure of many of the components, could they be isolated without decomposition, would undoubtedly prove to be of great scientific value.

Available Methods of Separation. At the present day there are several methods available for separating groups of components. Some industrial methods separate marketable groups of hydrocarbons, some of which may have existed in the naturally occurring oil, while others may have been produced by the treatment to which the crude oil was subjected while passing through the processes. Other industrial methods remove groups of constituents considered undesirable for the various purposes for which those marketable groups are being removed. These industrial processes are in principle mainly the same as were originally employed by James Young in 1850. Publications on petroleum refining invariably outline the processes from the view point of suitability for the production of fuels, illuminants, and lubricants, so that any systematic endeavour to separate individual components must be preceded by a critical experimental study of industrial processes from the view point of chemical analyst.

Before commencing these experiments a brief general survey of all the principal methods of separation, industrial and otherwise, is desirable.

Physical methods may be divided into three classes according to the principles involved, viz:-

Distillation.

Differential solvent action.

Diffusion.

Distillation:- When petroleum is distilled under atmospheric pressure there is, as one would expect, a gradual increase in boiling point while the distillates steadily increase in specific gravity. At about 325°C.[8] however, the temperature of the vapours remains constant or may begin to decrease, and the specific gravities of the distillates are correspondingly lower. This pyrolysis or "cracking" of the hydrocarbon molecule has been represented[9] by the equation

$$C_nH_{2n+2} \longrightarrow C_{n-p}H_{2(n-p)+2} + C_pH_{2p}$$

When such decomposition is undesirable steam may be introduced during distillation. By this means hydrocarbons which would normally undergo "cracking" during distillation are not only vaporised at a lower temperature because of the partial pressure of the steam, but are mechanically carried away from the hot zone in the current of steam as soon as they are evolved. This reduces the probability of subsequent "cracking" very considerably. In other cases, as, for example, in the production of lubricating oils a similar result may be obtained by distillation under reduced pressure.

In large scale operations cylindrical stills constructed of boiler plates rivetted together, have with advantage been arranged in batteries of, say, five, in such a manner as to supply the second still continuously with oil from the bottom of the first, the third from the bottom of the second and so on. By this means the distillates from each still remain practically constant in specific gravity but are progressively heavier from still No.I to still No.5.

High temperature vapours from still No.5, for example, may be passed around the crude oil pipe which feeds still No.1, so effecting economy by heat exchange before the vapours are finally condensed.

The last stages of petroleum distillation are usually carried out in "pot" stills of the older intermittent type, the bottoms of which are cast in one piece, because the oil is then too viscous for continuous automatic feeding and also because carbon or pitch is deposited in comparatively large quantities. This pitch may be heated to dryness before the completion of the distillation and stills must be suitable for this purpose as well as for the subsequent removal by hand, of the residual coke.

In common with other distillation processes more complete fractionation is effected by employing special "still-heads" or fractionating columns though one must remember that when dealing with petroleum, should these have the effect of retaining vapours for some time at a high temperature, or of causing condensed vapours to drop back into the still, a greater amount of "cracking" takes place.

Recently more complete fractionation has been effected by fractional condensation of the vapours. To effect this, first air coolers may be employed, followed by hot water, and ultimately cold water condensers, distillates being removed immediately after the vapours have passed through each type.

When certain of the higher distillates cool, solid hydrocarbons crystallise out, and separation of these is effected by filtration under pressure, followed by fractional fusion, to remove adherent oil. These solid hydrocarbons are usually decolourised by animal charcoal, bauxite, or other forms of alumina.

Differential solvent action:- Lessing[10] removed oil from coal tar by extraction with benzine free from aromatic compounds, leaving a pitch. The oil and pitch both differed from those obtained by distilling the coal tar.

Edeleanu[11] has successfully removed aromatic and unsaturated compounds from petroleum distillates by extraction with liquid sulphur dioxide.

Dimethyl sulphate has been suggested[12] for separating certain aromatic compounds. Its application is limited however, and it is extremely poisonous.

Alcohol mixed with various liquids, principally ether, has been employed[13] to wash crystalline paraffin wax free from adherent oil.

Carbon tetrachloride[14] and acetic anhydride have also been used as differentiating solvents, because of the relatively greater insolubility of certain solid components in them.

The naphtha distillate from crude oil was formerly employed in petroleum refineries for removing adherent oil from crude wax.

Of these methods Edeleanu's process and the naphtha treatment of crude wax are the only ones which have been found applicable to the systematic fractionation of crude mineral oil.

Should suitable solvents be discovered however, differential solvent action would undoubtedly be of great value for separating, undecomposed, the complex compounds and mixtures contained in petroleum.

Diffusion:- It has already been stated that petroleum may be considerably altered during migration through certain soils. Relative to this, Day and his co-workers[15.] have observed that (1) " when petroleum is "allowed to rise in a tube packed with fuller's earth, "there is a decided fractionation of the oil, the fraction "at the top of the tube being of lower specific gravity "than that at the bottom: (2) when water is added to "fuller's earth which contains petroleum, the oil which "is displaced first, differs in specific gravity from "that which is displaced afterwards, when more water is "added: (3) when petroleum is allowed to rise in a tube "packed with fuller's earth, the paraffin hydrocarbons "tend to collect in the lightest fraction at the top of "the tube, and the unsaturated hydrocarbons at the bottom". In this respect Floridin is said to be similar in action to fuller's earth.

No further work along these lines has been recorded, yet the proper application of the principles involved would, like differential solvent action, prove of great value for separating components as they exist in crude mineral oils.

Chemical Methods:- Chemical methods have been employed in the endeavour to estimate the amounts of various series of hydrocarbons in crude mineral oil. Of these, the most important are the removal of unsaturated compounds by concentrated sulphuric acid, followed by the removal of aromatic compounds by oleum.[16] Nastjukoff[17] states that formaldehyde in the presence of sulphuric acid forms, with unsaturated cyclic compounds, condensation products which are precipitated. As the manner in which many components of crude oil react with these acids is not yet known, and as there is overlapping of the action of the acids on known members of the series, the separation of even one class of components by chemical means is still a matter of great difficulty.

The working out of a successful method for this purpose would be of great importance from the view-point of chemical research.

# Part I.

## Experimental Study of Industrial Processes.

A sample of Burma crude oil was refined by the usual industrial methods for the purpose of studying the processes from the point of view of the chemist.

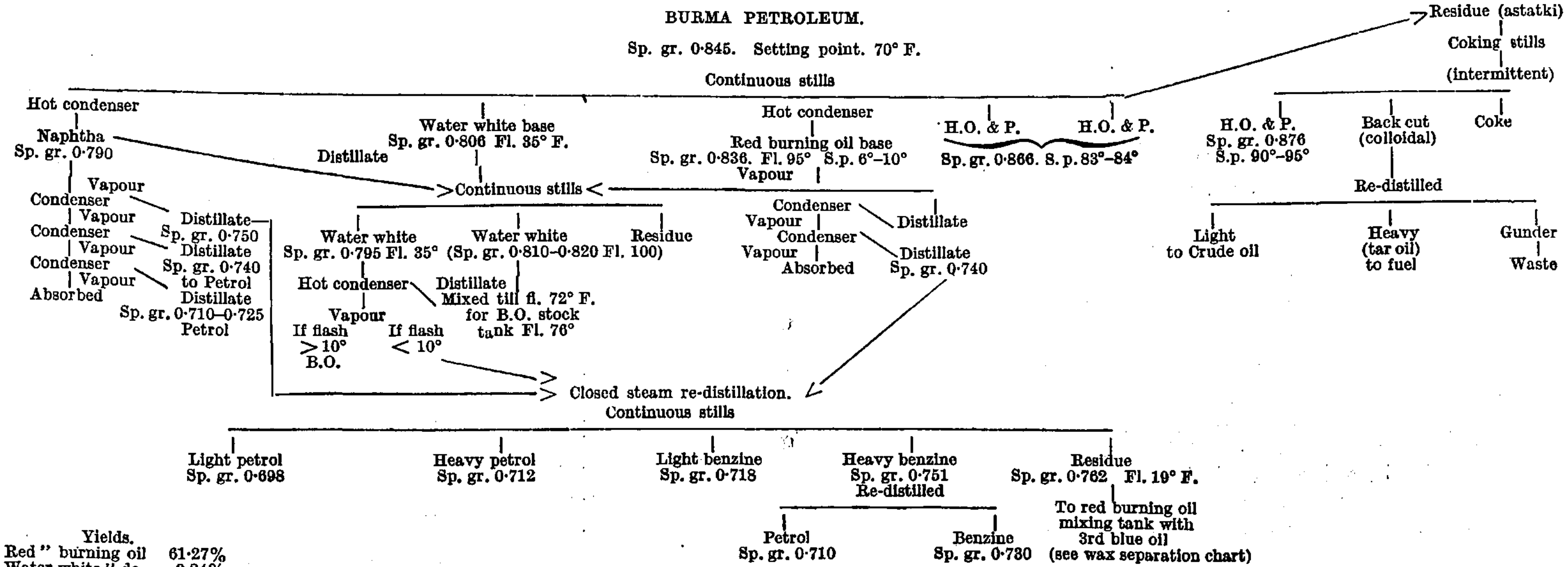
Distillation. The crude oil distillation plant consisted of a battery of six continuous stills of the Henderson type, one of which it was found necessary to retain empty, but ready for use in case of emergency arising out of trouble with any one of the others, from causes which will be described later. Twenty-four 'coking' stills were employed in conjunction with this battery. The first four continuous stills were connected in series: still No.5 was worked in parallel with No.4, as the fraction obtainable at the temperature attained in this still was found to be sufficiently large to require this increase in capacity. The crude oil was settled free from mud and water before the commencement of distillation as these gave rise to bumping and frothing in the stills. The oil then had Sp.Gr. 0.845 and Setting Point 70°F.

Burma petroleum is a "paraffin base" oil, and in these experiments distillation was so conducted as to

## *Crude Oil Fractionation.*

BURMA PETROLEUM.

Sp. gr. 0·845. Setting point. 70° F.



| Yields. | | |
|---|---|---|
| "Red" burning oil | 61·27% | |
| "Water white" do. | 9·24% | |
| Paraffin wax .. | 7·75% | See wax separation chart |
| Blue oil (for fuel) .. | 3·96% | |
| Tar oil .. .. | 0·16% | |
| Petrol .. .. | 1·87% | |
| Benzine .. .. | 6·88% | |
| Loss .. .. | 8·87% | |
| | 100·00% | |

produce distillates which contained a maximum quantity of crystalline paraffin wax, while endeavour was also made to separate petrol, benzine, and illuminating oil from each other, and illuminating oil from the Heavy oil containing Paraffin wax (H.O.& P.).

The modus operandi during distillation is outlined in chart form on the opposite page.

Heating was effected by burning heavy oil "atomised" by steam while spraying through a specially constructed nozzle in presence of an induced air draught.

At the commencement of distillation all five continuous stills were charged with crude oil and first distillates from all were therefore similar, but as each still following the first was continuously recharged with oil from which one or more lighter fractions had already been removed, the gravities of each steadily increased to a maximum which remained constant for a given furnace temperature below the still. Steam was introduced into each still; the quantity of steam and the furnace temperature being regulated in the manner described below.

In order to bring about the most efficient fractionation of petroleum by modern industrial processes it was found that the manipulation of each still, the arrangement of fractional condensers, the substitution of fractional condensation by redistillation, the distribution of semi-refined fractions for further treatment etc. had to be determined for each type of oil.

In the account given below of the manipulation of stills, the author describes the arrangement of the various methods he found to give the most satisfactory yields of products desired, from an average sample of Burma crude oil, and his reasons for adopting such arrangement.

Continuous Still, No.I.:- The distillate from the first continuous still should contain the entire 'petrol' content of the crude oil, and as far as possible all of the 'benzine'. It was not found possible to cut off this fraction so sharply as to be perfectly certain that it contained all of the benzine and no components suitable for admixture with illuminating oil. In order to remove any heavier components the vapour pipe was first passed through a condenser containing boiling water this having been found sufficiently cold to condense them. They had a Sp.Gr. 0.790 and were mixed with the distillate from No.2 still. 'Lighter' vapours passed on without condensation to warm water condensers which removed components having an average Sp.Gr. 0.750. This fraction was retained for careful redistillation by closed steam to remove any petrol. Remaining vapours passed successively through two sets of cold water condensers the former removing 'heavy petrol' of Sp.Gr. 0.740

and the latter 'light petrol' of Sp.Gr. 0.710 - 0.725. The end of the vapour pipe from the latter was immersed in heavy oil to absorb any so called 'permanent gas'. While the presence of '0.790 naphtha' was useful as an indication that, as far as possible, all petrol and benzine were being removed from the crude oil, the temperature of furnace No.1 was regulated so that the proportion of naphtha was not at any time a large one. The production of much permanent gas, indicative of cracking, was countered by the passing of more steam into the oil in the still.

Continuous Still No.2.:- It was found that the main portion of distillate No.2 was eminently suited for use as an illuminating oil. It contained however, small quantities of 'Naphtha', and of components too heavy for inclusion in a first grade kerosene: its Sp.Gr. was 0.806 and Fl.Pt.35°F. In order to ensure the most complete removal of these 'impurities' and of colouring matter, fractional condensation was supplanted by complete redistillation. As has been stated it was mixed with '0.790 Naphtha' from No.1 before redistillation: to these the lightest portion of distillate No.3 was added.

Because of the presence of the Naphtha, the first fraction of the redistillation was subjected to fractional condensation by employing first hot and then cold water condensers. Hot condensers removed a good quality oil of Sp.Gr. 0.795 and Fl.Pt.35°F. The flash point was too low to permit of its being employed alone as an illuminant, but was sufficiently high to allow its admixture in small quantity with the next fraction. The light vapours not condensed by hot water yielded, on condensation by the cold condensers, an oil which varied according to the amount of Naphtha present in the charge. If its flash point was below 10°F. it was once more distilled, this time by closed steam to remove petrol; if the flash point was above 10°F. it could be mixed with heavy benzine or with second grade illuminating oil, according as ite specific gravity was low or high. The proportion of oil flashing below 10°F. at this point could be raised by reducing the amount of steam entering No.2 Still so causing cracking. To produce the best quality illuminating oil however, cracking at this stage was kept at a minimum.

The main bulk of the first grade, or 'water-white' oil was obtained in the second fraction from this redistillation; its amount was regulated so that the oil was perfectly colourless, had Sp.Gr. 0.810 - 0.820 and Fl.Pt. about 100°F. Admixture with the first fraction reduced the flash point considerably, though never below the Board of Trade minimum for illuminants, but the specific gravity was only reduced to 0.806 - 0.810. Any residue from redistillation was periodically removed for chemical treatment and subsequent mixing with second grade illuminating oil. If the quantity of the residue became at any time excessive, the reduction of the temperature of furnace No.2 brought about the necessary diminution in bulk.

Continuous Still No.3.:- The third distillate furnished the base for the production of a second grade illuminating oil, heavier than the 'water-white' oil. Hot water condensed the greater part of this fraction, yielding an oil pale yellow in colour, having Sp.Gr. 0.836, Fl.Pt.95°F., and setting at 6°- 10°F. A cooler condenser removed a colourless oil similar to the water-white base previously described, with which it was therefore mixed. Further condensation by cold water removed a'benzine' fraction having Sp.Gr. 0.740 probably produced by cracking. This benzine was submitted to closed steam redistillation to remove petrol. Cracking having been indicated, immersion in heavy oil of the end of the vapour pipe from the last condensation was again rendered necessary as 'permanent gas' may also be thus produced. Cracking to the proper extent at this stage increased the yield of illuminating oil, but care had to be taken to prevent excessive cracking for reasons given in the description of the manipulation of the next two stages.

Cracking was again regulated by adjusting the amount of steam entering the still; while the setting point of the distillate, indicative of the amount of wax distilling at this stage, was kept at from 6° - 10°F. by adjustment of the furnace temperature. It may be considered by some that the setting point should be still further reduced in order to allow this wax to pass to H.O.& P. from which it would subsequently be removed, and also because the presence of wax is undesirable in an illuminating oil fraction. After many experiments, however, the author found that the further reduction of the setting point of this fraction brought about the transfer of so large a quantity of burning into H.O.& P. as to cause the latter to retain much wax in solution. This, it was found, involved an altogether disproportionate amount of subsequent refrigeration, for not only had a greater quantity of oil to be cooled, but the temperature of this oil had to be considerably lower than was otherwise necessary to bring about crystallisation of the wax.

Continuous Stills Nos.4 and 5.:- From this petroleum it was found possible to employ stills Nos. 4 and 5 for the exclusive purpose of removing heavy oil containing crystalline paraffin wax. That illuminating oil was excluded had been made certain during the collection of the previous fraction. At this stage great care had to be taken to adjust cracking, for the amount of crystalline wax obtainable from the oil increased in direct proportion to the amount of cracking up to a certain point, beyond which the percentage of wax produced, steadily diminished. The author has endeavoured to account for this by later experiments.(vide p.53. ) Vapours from these stills were cooled by water kept at boiling point by the vapours themselves. Further reduction in temperature tended to cause choking of the vapour pipe by the separation of solid wax. Distillates obtained in this way had average Sp.Gr. 0.866 and Setting Point 83°- 84°F. All of the H.O.& P. obtainable from the oil was not removed in continuous stills for two main reasons. First, the amount of necessary cracking which takes place during the removal of the heavier portion of H.O.& P. liberates carbon; for reasons given below this is undesirable in continuous stills. Second, the intrinsic value of the wax renders necessary the separation of all possible H.O.& P. Yet should any of the next fraction pass into H.O.& P., the separation of wax from the latter by refrigeration and filtration under pressure is impossible. By removing the last portion of H.O.& P. separately, this part only would have to be redistilled should any of the succeeding fraction inadvertently pass into the H.O.& P. receiver.

"Coking" Stills:- The last stages of the distillation were conducted in the usual way in intermittent stills. In these carbon was deposited in comparatively large quantity. After the last portion of the H.O.& P. (which was crystalline in structure when cooled, and had Sp.Gr. 0.876, and Setting Pt. 90°- 95°F.) had passed over, an amorphous gummy mass was obtained leaving a dry porous coke as residue in the still. After cooling, this was chipped out by hand.

Redistillation of the gummy material gave a mobile oil, probably produced by cracking, which was returned to the crude oil; a tar which was used as fuel, and a deep red-coloured resin the surface of which turned black on exposure.

Closed Steam Redistillation:- The lighter portions of distillates 1, 2, and 3 were mixed before redistillation by closed steam in continuous stills. Four main fractions were obtainable from the mixture, namely, 'light petrol' Sp.Gr. 0.698, 'heavy petrol' Sp.Gr. 0.712, 'light benzine' Sp.Gr. 0.718, and 'heavy benzine' Sp.Gr. 0.751. Even closed steam distillation produced pyrolysis for further redistillation of the 'heavy' benzine yielded a petrol of Sp.Gr. 0.710 and Benzine having Sp.Gr. 0.730. The residue from closed steam distillation had an average

Sp.Gr. 0.762 and Fl.Pt.19°F. These were mixed with second grade illuminating oil.

General Remarks:- Even with careful operation considerable loss took place during distillation owing to pyrolysis. In spite of agitation by steam, carbon adhered to rivets and at the junction of plates in continuous stills. This caused local superheating and possible absorption of carbon by the metal, followed by bulging of the still bottom and shearing of the rivets, resulting in the leakage of oil into the furnace below. For these reasons mainly, a spare still had to be in constant readiness as a substitute.

Recent methods to protect still bottoms from carbon deposition have been mainly mechanical, as, for example, the placing on them of iron chains to which carbon may preferentially adhere. From a chemical point of view catalytic hydrogenation would be more satisfactory.

Fractional condensation of vapours was found a useful improvement, but required efficient baffle devices to prevent the blowing over of 'heavy' vapours to a cold ('light'vapour) condenser in the event of 'bumping' taking place in the still.

The tendency of steam to carry a spray of unvaporised oil into the vapour pipe necessitated the interposition of baffle boxes or dephlegmators to trap drops of liquid hydrocarbons, particularly during the distillation of the heavier fractions.

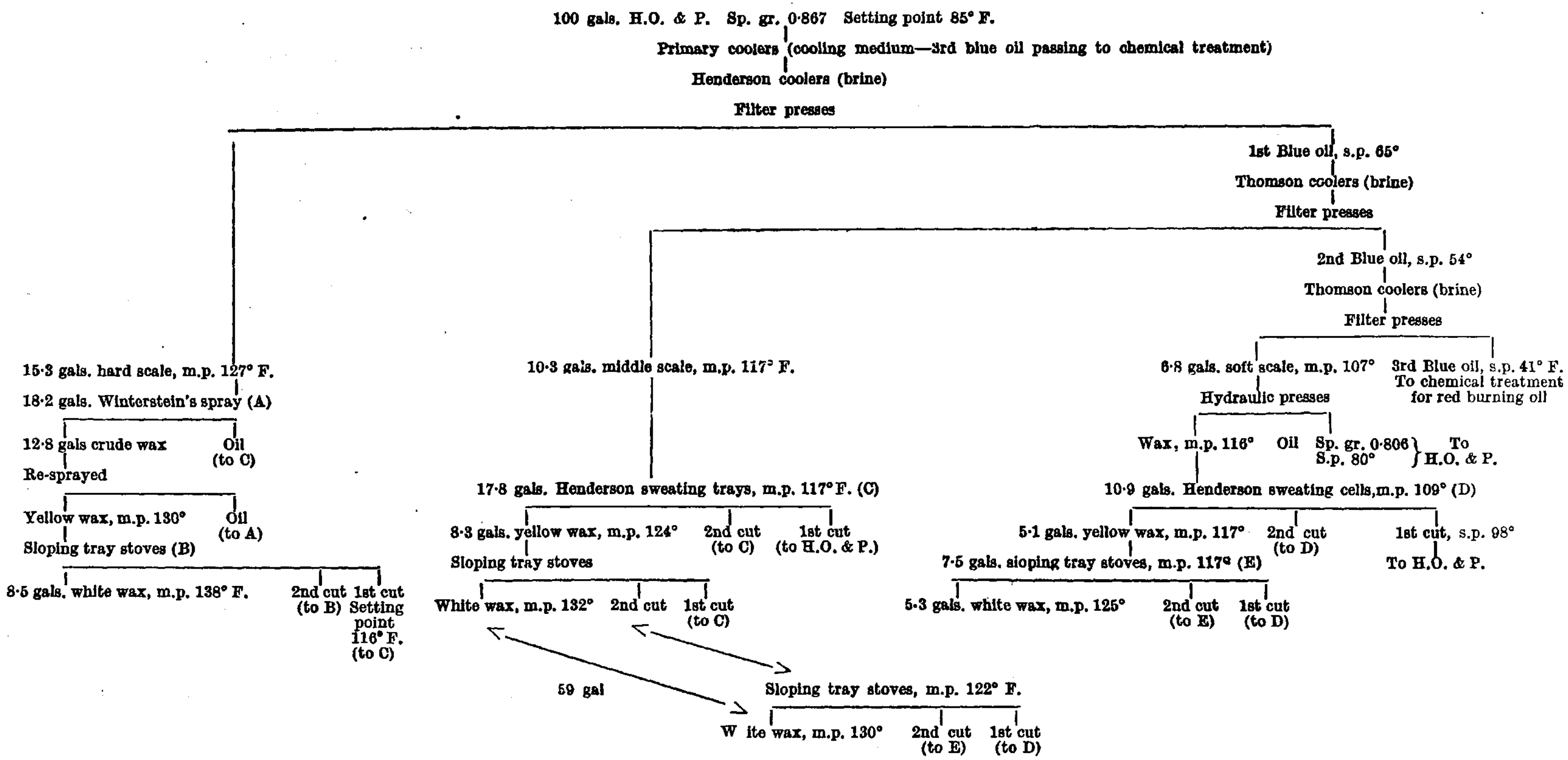
The principle of heat exchange utilised in the small preheater by which high temperature vapours are caused to pass around the pipe through which incoming crude oil is led, could be applied to a much greater extent than is done at present. The large quantities of cold water cirdulating through cooling apparatus should be substituted as far as possible by cold crude oil in 'closed' condensers, in the warmest of which fractionation would take place: to these, vapour pipes could be connected and led through condensers filled with colder crude oil. Lighter distillates would thus be collected before distillation by direct firing commenced.

It has been stated (vide p.4 ) that distillation cannot separate azeotropic mixtures, nor components of different type which boil at approximately the same temperature. It is now obvious from the above study, that few components are separated without decomposition, particularly in large scale operations, carbon being liberated even in the lower temperature stills employed for crude oil distillation, and pyrolysis occurring during closed steam redistillation of benzine.

Separation of Paraffin Wax. All three fractions

## *Separation of Wax.*

### BURMA PETROLEUM.



Total yield :—19·7 gals. white wax from 100 gals. H.O. & P.
= 7·75 „ „ „ Crude oil

of heavy oil containing paraffin wax were mixed and submitted to the process outlined in chart form on the opposite page.

Three types of refrigerating plant were employed by which to bring about crystallisation of the wax, namely, Henderson's Coolers, Thomson's Coolers, and a set of double jacketed cylindrical tanks containing scraper-stirrers, constructed to utilise cold 'blue' oil for precooling incoming H.O.& P. These precoolers reduced the temperature of the oil by about 7°F. Although wax separated in the precoolers it was not immediately removed by filtration, but was pumped directly into Henderson's Coolers which were found capable of working satisfactorily with very viscous material. In these the temperature was reduced by about 13°F. after which the oil was pumped under a pressure of about 100 lbs./sq.in. through horizontal filterpresses. Cooling was effected slowly throughout, in order to obtain a thoroughly crystalline wax from which oil would easily separate during pressure filtration.

The press room was cooled to prevent wax redissolving in the oil during filtration, but its temperature was never less than 2°F. higher than the temperature of the incoming oil. This precluded the possibility of clogging the pores of the filtercloth by crystals of wax deposited in situ. This filtration removed 15.3 % of crude scale M.P.127°F. from the heavy oil. The blue oil filtrate was pumped through a series of Thomson's Coolers arranged in parallel, in which its temperature was reduced 11°F. Continuous coolers of the Thomson type are a decided improvement upon the older intermittent (Henderson) type from the point of view of large scale manipulation and throughput, but were not found perfectly satisfactory in certain other respects. The direct expansion of ammonia into the outer jacket caused, by excessive local cooling, the formation of a tube of solid wax inside, which rotated with the stirrers, and through which oil passed without great reduction in temperature. Circulation of cold brine through the outer annular space was, however, quite effective. When the coolers are arranged in parallel, one may become partially choked, causing excessive flow through, and inefficient cooling in the others. It was, therefore, found advisable to insert a thermometer at the base (exit) of each cooler. This rendered possible the adjustment of the rate of flow of brine and of oil through each cooler, so that the temperature of the outgoing oil from each was the same. The following temperatures were obtained immediately after the introduction of these thermometers and as a result cooler No.10 for example, was rendered more efficient by giving it relatively more brine and less oil, while coolers Nos. 14, 15, and 18 received slightly less brine and more oil.

Temperatures taken at exit from Thomson's Coolers when run in parallel.

| Cooler No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Temperature | 58° | 62° | 58° | 66° | 58° | 58° | 58° | 58° | 58° |
| Cooler No. | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| Temperature | 68° | 58° | 58° | 60° | 54° | 54° | 58° | 58° | 54° |

The oil exit pipes from these coolers are much too small in cross section relative to the size of the coolers, for the nature and quantity of material which passes through them. 10.3 % scale M.P. 117°F. was obtained by pressure filtration following this second cooling. The blue oil filtrate set at 54°F. Another set of Thomson Coolers reduced the temperature of the second blue oil from 54°F. to 41°F. causing the separation of 6.8 % scale M.P. 107°F. which was filtered off in the same manner as before. The filtrate set at 41°F.

The order in which continuous and intermittent coolers were respectively employed was determined by trial. First, precooled oil entered nine Thomson Coolers in parallel, and, after filtration, nine more Thomson Coolers. After a second filtration, the oil was finally cooled in nine of Henderson's intermittent type. Because of their tendency to jam, Thomson's coolers were not found suitable for the reception and further cooling of unfiltered, precooled, H.O.& P. The second set of these coolers would have proved quite suitable for chilling the filtrate from the first set, if the arrangement had permitted of a continuous flow of oil through the system. This was not possible however, for the intermittent coolers required so much time to effect the final low temperature cooling as occasionally to hold up oil in the continuous coolers where it tended to set to a solid mass.

The carrying out of the first and second coolings in one operation by putting all eighteen continuous coolers and their respective filter presses in parallel did not help matters, even when a blue oil tank was interposed between continuous and intermittent coolers to ensure a continuous flow through the continuous type. The blue oil accumulated, more especially when filter presses working in conjunction with continuous coolers were'empty', and those attached to intermittent coolers more or less filled with scale. The greater cooling power of the continuous coolers rendered their adoption for final cooling necessary for most effective working.

Henderson's Coolers could, however, effect the first cooling quickly enough to keep the Thomson's Coolers continuously supplied when the latter were employed for low temperature work. By this arrangement the most viscous mass was treated in coolers having a lesser tendency to jam.

The carrying out of the second and third coolings in one stage by again arranging eighteen Thomson's Coolers in parallel, was not satisfactory, because of the large amount of wax liberated by so great a reduction in temperature, again jamming the coolers. The second chilling was therefore carried out in nine Thomson's Coolers and after removal of suspended wax, the final cooling was effected by the remaining nine.

Refrigeration followed by pressure filtration does not remove such wax as dissolves in the oil at the temperature of the last cooling. This temperature is determined, in industrial work, by comparison of the cost of a further cooling with the market value of the wax, which would be so obtained. Third blue oil therefore, invariably contains wax in solution which cannot economically be removed. The crude wax or scale obtained by these methods always contains a fair proportion of adherent oil, some of which, in these experiments, commenced to ooze from the third or 'soft' scale as the latter rose to atmospheric temperature. The oil so liberated was expressed by vertical hydraulic presses. As a result the setting point of the 'soft' scale rose from 107° to 116°F. while the oil expressed had Sp.Gr.0.806 and Setting Point 80°F.

It is customary when speaking of scale, which is solid at ordinary temperature, to refer to its 'melting point'. While this custom has been adhered to in the chart depicting wax separation the author believes that the more accurate restriction of the term to solid hydrocarbons entirely free from oil would lead to more efficient working in the refinery. When one speaks of a scale 'melting' at 115°F. and of another 'melting' at 120°F., it is natural to conclude that the latter contains a mixture of relatively higher hydrocarbons, whereas , the high 'melting' point may be caused by a high percentage of lower hydrocarbons, with less adherent oil than the former. The so called melting point is really the solidifying temperature of a concentrated solution of wax in oil. This should be borne in mind when considering to what part of the process crude waxes or 'sweatings' should be returned if further treatment of these be necessary. The specific gravity should then be taken to determine the quantity of oil present. By hydrometer measurement of the liquid wax and oil respectively, and subsequent allowance for temperature, 'white' wax was never found to exceed 0.810 while third blue oil was about 0.880 at 60°F.

While the oil removed from soft scale by hydraulic presses had a setting point 80°F. and was, because of this, originally returned to H.O.& P. which had a similar setting point, the determination of the respective specific gravities showed at once that H.O.& P. contained high melting waxes with a large proportion of oil, while the 'oil' from soft scale was mainly wax of low melting point. When cooled together with H.O.& P. to 65°F. the low melting solids from soft scale would be removed and filtered off along with the high melting waxes present in the H.O.& P. and would pass to a high temperature sweating to be circulated throughout the process as sweatings. The alternative method of returning these low melting solids to the third cooling would have to be carried out gradually to avoid jamming and they would probably again be expressed in the hydraulic presses. The proper procedure in this case was therefore gentle separate sweating at low temperature for the removal of paraffin wax of low melting point.

Sweating. In these experiments, sweating was carried out by means of Henderson's 'stoves', Henderson's 'cells', sloping tray 'stoves', and Winterstein's 'spray'. Sloping tray stoves proved most efficient for the production of oil-free wax, as the slabs of wax after sweating could be hand picked free from oily patches before transference to the melting tank. They were therefore employed for sweating from 'yellow' to 'white' wax. By doubling the duration of this process the yield of 'white' from 'yellow' wax was increased by 2.5 %. The process involved less mechanical but much more manual work than the others.

In the event of unequal sweating in Henderson's 'tray stoves' or 'cells' oily patches could not conveniently be removed. Residual wax after melting was, further, contaminated by oil while flowing to the receiving tank over the bottom of the trays and through pipes, both of which were coated with the oily sweatings which had previously passed out from the wax.

For these reasons Henderson's plant was not employed for the production of white wax, but for sweating from scale to Yellow wax. Winterstein's spraying process was not found effective for the preparation of 'white' wax, neither was it found easy of application to very soft (low setting point) scales, where a low temperature spraying was required. It was therefore utilised here for the conversion of 'hard' scale into yellow wax. Even when so applied, the separation of water and of oil and the subsequent melting of the partially refined 'scale' occupied several hours; the time taken to spray 4,500 gallons of scale M.P. 52.2°C. was 1.5 hrs., to drain off oil and water 1.0 hr., to melt residual scale M.P.55.5°C. 3.0 hrs., and to pump off melted scale 1.0 hr. It was found necessary again to spray this wax in order to obtain a yellow wax of fair quality. The process however, seemed amenable both to modification and to improvement of such nature as would render possible at one spraying operation, the continuous production of 'yellow wax' from 'scale'. Many adjustments of the modus operandi were possible, so that wax of a better quality as well as an increase in the present relatively high yield could reasonably be aimed at.

In order first to speed up the process and subsequently thus to modify and improve it, the author in conjunction with R.S.Dickie endeavoured to remove water and oil from the sprayed mass by wrapping quantities of it in coarse filter cloth and pressing between perforated plates in a vertical hydraulic press. The cloths burst on every occasion before separation commenced. Rotation in a centrifugal machine proved no more effective. It was thought that the presence of water in intimate contact with the oil in the pores of the spongy mass of wax was preventing the filtration of the oil. Melted scale settled free from water was therefore sprayed with cold gas instead of water. The nozzle employed was similar in construction to that of ordinary coal gas - air blow pipe. A cylinder of Carbon Dioxide under pressure was connected with the air blast and after spraying of oil with air had commenced, carbon dioxide was allowed to expand in the air pipe, so reducing the temperature of the issuing oil-gas mixture to 3°C. below the setting point of the scale. A pale yellow spongy mass was at once obtained from which oil rapidly separated. By receiving the sprayed scale in a rotating centrifugal machine a good quality 'yellow wax' was immediately obtained.

The following table shows the results obtained.

| | Scale. | | Oil removed. | |
|---|---|---|---|---|
| | M.P. °C. | Sp.Gr. (15.9°C.) | Setting pt. °C. | Sp.Gr. |
| 1. Scale taken | 40.0 | 0.825 | | |
| 2. Pressed at 25.5°C. | 42.8 | 0.820 | 26.6 | 0.861 |
| 3. Sprayed with air | 44.4 | 0.812 | | |
| 4. Centrifuged | 45.5 | 0.811 | 33.3 | 0.840 |
| 5. Again pressed at 25.5°C. | 46.1 | 0.810 | 25.0 | 0.857 |

It will be observed that while the pressing of crude scale raises the melting point only 2.8°, spraying with air followed by pressing raises the melting point 6.1° and is therefore as effective as sweating, while occupying approximately one tenth of the time. The oils expressed have all comparatively high specific gravity, and correspond roughly with the first cut obtained by sweating. The objectionable middle cut cycle referred to below has therefore been removed.

The present process for wax separation has been described as efficient.[18] This is contrary to the author's experience. During the sweating of the crude scale, for example, oil oozes out of the wax, but the wax is soluble to a certain extent in this oil and some is naturally carried away in solution. It was found that as sweating proceeds the percentage of wax in the sweatings increases, due, no doubt to the fusion of waxes of low melting point as well as to the solution of wax in oil. Because of this, sweatings have to be collected in two fractions or 'cuts'. The first cut from scale sweating usually contains approximately the same percentage of wax as the original H.O.& P. with which it is therefore mixed. This necessitates its passage through the refrigeration and sweating processes once again. The second cut from scale sweating has approximately the same wax content as the original scale charge and must therefore be returned to the charging tank to be sweated again. For similar reasons the first 'cut' from yellow wax is returned to scale, the second 'cut' to the yellow wax tank.

Roughly two thirds of the working capacity is being taken up by the returning of material which has already been through the process and much of which is probably again returned on reaching the same state of refinement as before. In the end some oil has to be removed from the sweating process, and this is bound to contain more or less wax which is not only then lost, but is detrimental to the material with which it is mixed, whether this be burning oil or lubricating base.

During the wax removal there is a large waste of energy by heat exchange. Thus any portion of heavy oil during refining operations is heated during the first distillation; cooled from vapour to semi-solid, warmed till fluid enough to be pumped to the wax removal department, then cooled to allow the wax to crystallise; the crude wax is melted and run into tins or trays to cool before sweating, heated during sweating, sweatings after cooling are again distilled; finally, the sweated wax is cooled and cast into slabs for the market. This repetition of heating and cooling could surely be obviated.

Decolorisation. For the final decolorisation of 'white' wax, agitation of the melted wax with animal charcoal ('ferrocyanide' char) was found much superior to similar treatment with vegetable char, but vegetable matter carbonised after soaking in zinc chloride solution

## Analyses of Naturally Occurring Earth found suitable for decolorising Paraffin Wax.

| | Sample I. | Sample II. |
|---|---|---|
| Moisture | 0.90 % | 0.92 % |
| Sand and Siliceous matter | 61.53 % | 51.79 % |
| $Fe_2O_3$ | 3.40 % | 20.55 % |
| $Al_2O_3$ | 30.94 % | 23.06 % |
| $CaO$<br>$TiO_2$ | Trace | Trace |
| Organic matter | 3.15 % | 3.63 % |

and subsequently washed free from zinc chloride gave quite good results. It was found that 'ferrocyanide' char which had been employed for the final decolorisation of a white wax was quite suitable for partially decolorising a more highly coloured wax. A counter-current system was therefore employed, thus effecting economy in decolorising carbon. A naturally occurring earth nearly white in colour, analyses of which are appended, also removed colour on stirring with the melted wax. The complete recovery of adherent wax from decolorising carbon after use proved difficult. Filtration through steam jacketed filter-presses followed by extraction in a Soxhlet apparatus left a carbon from which, after drying in a steam oven, more wax could be extracted by boiling benzine. An apparatus was therefore devised which would at once remove moisture and thoroughly extract wax from large quantities of spent char with boiling solvent. The spent decolorising carbon was placed in a wire gauze container lined with filter cloth and the whole enclosed in an iron tank. Superheated benzine vapour was caused to enter at the bottom of the tank, and to pass through and around the carbon, carrying any moisture upwards with it as vapour, to a reflux condenser. The condensed benzine and water were received in a separator, and benzine alone overflowed into the extractor. Piping was so arranged that the liquid benzine flowing to the extracting chamber was kept at boiling point by the up-passing benzine vapour. The boiling benzine was distributed over the carbon, through which it percolated, dissolving wax. Thence it returned to the super-heater where most of the benzine was again volatilised, and melted wax alone ran back to the still. After extraction the reflux condensation was stopped; the benzine vapour from the still passed directly to the condenser, the distillate being received in the separator, whence benzine overflowed into a tank employed to charge the still. Heating was carried out entirely by closed steam until practically only wax remained in the still, when open steam was used to remove the last traces of benzine. The wax was then run from the still to a receiver. While distilling off benzine from wax after extraction, the extracting chamber was completely cut off from the remainder of the plant in order that it might be emptied and recharged. This plant treated about 8,000 lbs. of char at each charge and was successfully operated in batteries, each containing five extractors.

Prior to the construction of this plant a large amount of wax was lost, because it had been found possible to recondition spent 'ferrocyanide' char by baking for a few hours in a low temperature muffle furnace. After this treatment the char recovered about three fourths of its decolorising power, but all adherent wax was destroyed in the furnace.

Chemical Treatment. Treatment of oils with concentrated sulphuric acid for the removal of olefines and diolefines, aromatic and oxidisable compounds, followed by treatment with caustic soda solution for removing phenols, naphthenic acids etc. was effective, but all these materials were then lost for practical purposes except as fuel, the tars formed being of extremely complex and at present unknown composition.

As an example of the efficacy of the process, however, the author found that, by the following method only 1 % of sulphuric acid was necessary to render a typical third 'blue' oil from Burma H.O.& P., pale red and transparent. This quantity, the author believes, is considerable less than is usually employed for the acid treatment of a heavy and dark coloured oil. 'Blue' oil (4,500 galls.) Sp.Gr.0.881, Flash Pt. 150.5°F., Setting Pt. 44°F., was mixed with 0.17 % of sulphuric acid, agitated by air, and allowed to settle for 30 mins., the tar was run off, 0.33 % of acid added and the tar immediately run off; 0.50 % of acid was then added and the mixture agitated for six hours, allowed to settle for seven hours, and the tar run off. Caustic soda was then added in quantity little more than sufficient to neutralise excess acid, the mixture was agitated for 30 mins., allowed to settle for 30 mins., and the tar run off. After agitation with water for half hour periods till no alkaline reaction to phenolphthalein was shown, the treated oil had Sp.Gr. 0.841, Flash Pt.142°F., Setting Pt. 44°F.

# Part II.

## (a) Physical State of Components in Naturally Occurring Crude Oil.

## (b) Fractional Precipitation as a Means of Separating Groups of Components without Decomposition.

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(a) The foregoing study of industrial processes makes quite clear to the chemist the futility of any endeavour to separate individual components without decomposition, by mere improvement of the existing large scale methods. Before attempting to employ methods involving new principles a better knowledge than we possess at present of the physical state of the components as they exist in the naturally occurring crude oil, is necessary.

An attempt by the author to remove solid paraffins from crude petroleum, without distillation, by direct refrigeration and filtration under pressure, resulted in the production of an amorphous pasty mass, which could not, by pressure, be freed from the large quantity of adhering oil. A similar product obtained by high speed centrifuging instead of pressing has since been seen by the author, who had previously endeavoured, but without success, to separate wax from its concentrated solution in oil (melted crude scale) by means of a De Laval cream separator. It would seem from these results that the physical state of solid hydrocarbons in crude oil is quite different from that of the wax in melted crude scale. Distillation has apparently brought about this change for the fibrous crystalline wax in cooled distillates is quite unlike the amorphous product from cooled crude oil. It was therefore assumed that some of the components may exist in a colloidal condition in crude oil.

<u>Optical Examination</u>.

An optical examination of several crude oils was made. The light from a carbon arc was passed through a collecting lens, a precision slit, and a focussing lens so as to cause a fine intense pencil of light to enter the oil contained in a small clear silica cubical cell. Anglo-Persian crude oil and Hardstoft crude oil, representing totally different types, each showed a distinct unbroken Tyndall Cone. This cone, viewed through a Nicol's prism disappeared on rotating the prism, reappearing at a certain angle, thus proving that the cone was not due to fluorescence. Ultra-microscopic examination was then made. A brass tube 80 mm. long, 15 mm. in diameter, closed at one end, and lined with glass was constructed. This was filled with Anglo-Persian crude oil, and the open end closed by a glass disc and brass screw cap. A hole 1 mm. in diameter had been bored through the screw cap and a similar one through the side of the brass tube near the cap. The pencil of light obtained in the manner described above was passed through a small telescope so that a very fine but intensely bright beam passed through the hole in the screw cap. The cone formed in the oil was viewed through a high power microscope placed over the hole in the side of the brass tube. The dark coloured Anglo-Persian 'crude' showed a distinct disperse phase, but the brown translucent 'crude' from Hardstoft did not give rise to the same scattering of the light. In the former case the phenomenon may have been due to colloidal asphaltic material, while the colloidal components in Hardstoft 'crude' may all have a refractive index approximating too closely to that of their dispersion medium to cause the same scattering of light.

It was thought that the Tyndall phenomenon, so clearly shown by both 'crudes' might be due to the colloidal or emulsoid condition of associated hydrocarbons, and of those components having complex molecules, in a dispersion medium of lower hydrocarbons, the degree of association becoming less as the homologous series are descended until a molecular dispersion (true solution) is reached among the lower hydrocarbons. A study was therefore made of the behaviour of various oils when subjected to the ordinary processes for the coagulation of colloids.

## Electroendosmosis and Kataphoresis.

A porous pot containing Anglo-Persian crude oil Sp.Gr. 0.8847 at 15°C. was surrounded by the same oil contained in a beaker. Platinum electrodes having a potential difference of 250 volts were suspended in the oil, inside, and around the porous pot respectively, for 20 hours. No migration of particles through the pores of the pot took place as the physical constants of the oil in and around the pot remained the same.

In order to aid both coagulation of colloidal material and the passage of the electric current, 25 cc. of 1 % absolute alcoholic Potassium Acetate were added to 250 cc. crude oil. The oil was placed in a U tube and no membrane was interposed between the limbs. The plumet of a Westphal balance was suspended in each limb so that any change in specific gravity would be immediately observed. An electro-motive force of 4 volts produced no change after 12 hours.

In order further to aid coagulation, the salt of a tervalent electropositive element was introduced, a solution of ferric chloride in ether being substituted for alcoholic potassium acetate. No result was produced by a difference in potential of 4 volts after 3.5 days.

The method was then modified by carefully introducing Hardstoft crude oil at the base of a U tube partly filled with absolute alcohol. A difference of potential of 250 volts was sustained between electrodes immersed in the upper alcohol layer, for 7 days. No difference in the level, nor in the composition of the oil in each limb was detected. This experiment was repeated with heavy dark cylinder lubricating oil instead of Hardstoft 'crude', but diffusion of oil into alcohol was the only change. A further modification was made by superimposing 90 % alcohol on an oil-aqueous soap emulsion. The breaking down of the emulsion into well defined layers of aqueous soap solution, and oil, respectively, was the only result.

While high centrifugal force separates an amorphous mass from the crude oil, it would appear from these experiments that petroleum colloids exist in a very stable form; or it may be that the colloidal state was changed to one of true solution either by the action of the solvents, containing electrolytes, which were added, or by the action of the electric current. That the former is possible will be observed from subsequent experiments.

## Dialysis.

Dialysis was attempted by surrounding with ether a parchment capsule containing Hardstoft crude oil.

After twelve hours, osmotic passage of ether into oil was found to have caused the capsule to overflow.

## Paraffin Wax from Undistilled Oil.

In order to recover and examine the oil from the surrounding ether, the solution was placed under a bell jar and the pressure reduced. Immediately after evaporation had reduced the temperature so far as to stop ebullition of the ether, white flakes began to separate. These were filtered off and found to be solid wax. A subsequent experiment showed that none of this wax had passed into the ether by dialysis. The flakes of wax had, therefore, separated from a solution of untreated crude oil in ether.

This separation of oil-free wax from undistilled petroleum is extremely interesting when compared with the oily amorphous mass previously obtained by direct treatment of crude oil. Schwarz[19] brought about a separation of wax from butanone by cooling the solution, but he originally dissolved crystalline wax. A.E.Dunstan says,[20] "Certain oils contain paraffin wax - not before "they are distilled, but after". It would now appear that paraffin wax does exist in certain oils before distillation but in a condition which is altered to the crystalline form by distillation; and that the dissolving of petroleum in a suitable solvent, such as ether, has an effect on the wax similar to that produced by distillation. This principle, suitably modifed and applied, should prove useful for separating without decomposition, not only solid from liquid hydrocarbons, but solid from other solid, and liquid from other liquid components. If instead of concentrating and cooling a solution of the oil, as above, successful additions of a third substance miscible with the solvent, but as far as possible immiscible with petroleum, be made, it is possible that a fractionation may take place.

### (b) Fractional Precipitation as a Means of Separating Groups of Components without Decomposition.

Alcohol-ether mixtures have been employed to wash wax, obtained by distillation, free from oil. The addition, to a solution of crude oil in ether, of successive quantities, first of alcohol then of water, might bring about the desired fractionation.

Qualitative tests confirmed this; first solid paraffin wax, then Hardstoft crude oil were successfully fractionated.

### Qualitative Fractionation of Paraffin Wax.

To a solution in ether of paraffin wax, M.P. 56°C. contained in a separating funnel having a false bottom of copper gauze, 90 % alcohol was added till sufficient precipitate had formed to carry out a melting point determination. The solution was run off, the gauze supporting precipitated wax removed, and dried in an air blast. The wax was detached from the gauze, pressed between filter papers and found to melt at 68°C., i.e. 12°C. higher than the wax originally dissolved.

## Qualitative Fractionation of Crude Oil.

Successive small quantities of 90 % alcohol were agitated with a solution of Hardstoft crude oil in ether, the precipitate being removed after each addition. When no further precipitation was produced by alcohol, water, acidified with sulphuric acid to prevent emulsification, was added. In this way fractions varying from a dark greenish-brown paste to a yellow very mobile liquid were obtained.

## Quantitative Fractionation of Hardstoft Crude Oil.

A quantitative fractionation of Hardstoft crude oil was carried out in the following manner, and the fractions examined.

250 cc. Hardstoft 'crude' at 15°C. taken.

Agitation by mechanical stirrer commenced.

500 cc. ether added, (temperature 10°C.)

### Fraction I.

275 cc. 90 % $C_2H_5OH$ added. Precipitation appeared to commence after 195 cc. $C_2H_5OH$ had been added.

Transfered to separating funnel, settled, and separated.

Fraction II.

200cc. $C_2H_5OH$ added, and treated as above. (Temp.12.5°C.)

Fraction III.

800cc. $C_2H_5OH$ added, and treated as above. (Temp.12.5°C.)

Fraction IV.

Equal volume of acidified water added, and treated as above, (Temp.22.8°C.)

In all 1,000 cc. Hardstoft 'crude' were fractionated in this way.

Ether was removed by drawing air through the fraction; alcohol by extraction with water which displaced more ether: air was again drawn through in presence of an excess of water. Such emulsion as had formed was destroyed by the immersion in it of electrodes between which existed an electrical potential difference of 250 volts, this having been found suitable for breaking up an oil-aqueous soap emulsion during the Cataphoresis experiments described above. After separation of the water layer the oil was finally dehydrated over granular calcium chloride.

The following constants of the four fractions were obtained:-

1,000 cc. Hardstoft crude petroleum Sp.Gr.0.8203 at 15°C. taken.

| | Vol. cc. | Sp.Gr. (60°F.) | Viscosity (Redwood 70°F.) | Flash Pt. °F. | Iodine value. (Wijs) |
|---|---|---|---|---|---|
| Fraction I. | 155 | 0.8468 | 5'45" | 94 | 2.63 |
| Fraction II. | 295 | 0.8398 | 2'40" | 92 | 3.37 |
| Fraction III. | 115 | 0.8349 | 2'30"* | 86 | 2.11 |
| Fraction IV. | 355 | 0.7966 | 35" | - | 2.92 |
| Total | 920 | | | | |
| Average Sp.Gr. | | 0.8237 | | | |

* Cup only half full.

It was presumed that a large part of the 8 % loss was due to the volatilisation of light components during the removal of ether; this, it was found, could be avoided by preliminary extraction of them, by absolute alcohol or glacial acetic acid, followed by precipitation from these solvents by the addition of water.

Other solvents and precipitants were tried with more or less success, a table giving the solubility of ozokerite in various liquids[21] proving a useful guide.

Reprecipitation of Fraction I. is necessary in order to obtain solid wax. In 1888 Van Bemmelen wrote[22] in connection with the coagulation of colloids into flakes: "I think it possible that the formation of flakes "which are precipitated in a liquid is dependent upon a "change in the surface tension of the liquid membrane "surrounding the colloid particle, of such type that "these membranes between the particles are torn at some "point, thus permitting the particles to form aggregates." It is not necessary, therefore, that solid hydrocarbons in petroleum should be different even in structure from crystalline paraffin wax in order to behave as they do. Their molecules or aggregations of molecules may be surrounded by a protective membrane of heavy liquid hydrocarbons in an emulsoid state. The reason why wax separates so readily from H.O.& P. and not from crude oil is presumably because there is no protective colloid in the former, this having been destroyed by the heat treatment. If the gummy 'back cut" or last fraction of a petroleum distillation be permitted to pass over into H.O.& P., separation of wax once more becomes impossible, yet the wax is crystalline. The difference lies only in the presence of the protective colloid. It has still to be proved, therefore, that there is such a substance as so-called 'proto-paraffin' in contradistinction to ordinary crystalline paraffin wax; heat treatment or solution in certain solvents is sufficient in these instances to rupture a protective membrane and so permit particles of solid hydrocarbon to form aggregates capable of separating out.

It will be remembered that, during the distillation of crude oil, the percentage of wax obtained increased in direct proportion to the amount of cracking which took place in the stills, but up to a certain point only, beyond which the amount of wax steadily diminished. This may be due to the breaking up of complex molecules by heat. The products of decomposition may be solid, or they may undergo internal molecular rearrangement, or chemical reaction with one another to form solids, further heat treatment subsequently decomposing the solids. An alternative or additional explanation is now possible. Pyrolysis may cause the rupture of protective membranes of heavy liquid hydrocarbons existing around crystalline wax originally present in the crude oil. This protective colloid having been removed, further pyrolysis would decompose the wax itself.

The fractionation of petroleum by precipitation is interesting in another respect from a 'colloidal' point of view. In each fractionation the first few fractions (I.,II.,and III.) were extremely viscous and the remainder (IV. in this separation) very mobile. This tendency was still noticeable when the proportions of solvent and precipitant were altered. There was no marked gradation in viscosity, such as is obtained by distillation. The viscous fractions behaved as emulsoids inasmuch as when violently shaken they became more mobile and after repeated shaking remained so for some time. It was thought that the viscous fractions might have a high iodine value, it being commonly stated that as a rule the higher fractions of petroleum contain a large percentage of unsaturated hydrocarbons. The iodine values of all four fractions were determined under identical conditions and were roughly the same and quite low. This may be a peculiarity of Hardstoft crude oil, or it may be possible that the unsaturated substances usually found may be produced at the high temperature employed for the removal of the higher fractions by distillation.

# Part III.

## (a) Fractional Emulsification.

## (b) Surface Tension.

The results of the investigation described in Part II. above directed attention to those surface phenomena so closely connected with the colloid state.

### Fractional Emulsification.

The following experiments were made to test the view that fractional emulsification might prove a suitable method for the separation of certain components without decomposition.

On agitating petroleum with water and allowing to stand until further separation of oil from water became inappreciable, running off the milky emulsion of oil in water, and repeating day after day, it was found that the specific gravity of the remaining oil was lower than that of the original petroleum. A point was ultimately reached when the specific gravity of the remaining oil increased slightly. This was considered to be due to the volatilisation of the lighter components by continued agitation.

| | | |
|---|---|---|
| Sp.Gr. of original crude oil | 0.8158 | at $15^\circ$C. |
| Sp.Gr. after shaking with distilled water for 5 minutes, settling and removing the emulsion. | 0.8150 | " |
| Sp.Gr. after again shaking with distilled water, settling for 12 hours, and separating. | 0.8145 | " |
| Do. repeated | 0.8148 | " |
| Do. do. | 0.8150 | " |
| Do. do. | 0.8149 | " |

At this stage a small quantity of soap solution was added. On agitating and separating the froth, and the emulsion, formed, the gravity of the oil from the froth was decidedly higher, and that from the emulsion very slightly higher than that of the original oil.

| | | |
|---|---|---|
| Residual oil after first emulsification experiments | Sp.Gr. | 0.8149 |
| Agitated with aqueous soap solution | | |
| Oil from emulsion so formed | Sp.Gr. | 0.8152 |
| Oil from froth so formed | " | 0.8268 |

A modification of these experiments was effected by sending a very fine spray of water downwards through a column of oil. The froth raised was evanescent but the emulsion formed was carried downwards by the stream of water and trapped in a receiver below from which water was allowed slowly to drain away. The specific gravity of the main bulk of oil was found to have dropped while that of the oil from the emulsion was higher.

| | |
|---|---|
| Sp.Gr. of original oil | 0.8441 at 15°C. |
| Do. after spraying and removing emulsion | 0.8438 " |
| Sp.Gr. of oil from emulsion | 0.8460 " |

Bayliss has examined the froth produced by agitation of an aqueous solution containing saponin and rennet.[23] The froth contained saponin only. Saponin lowers the surface tension of water more than rennet and apparently because of this is capable of displacing the latter from surface layers. Should one hydrocarbon lower the surface tension of a liquid (or solution), more than another, then the first hydrocarbon should displace the second from surface layers, either in a froth or surrounding globules of the given liquid suspended in the hydrocarbon mixture. Lewis, in this way, removed sodium glycocholate from aqueous solution at the surfaces of paraffin oil globules.[24.] It is possible therefore, that the surfaces of globules of sodium glycocholate solution, or some other substance, may prove suitable for the removal of higher components from solution in the lower components of paraffin oil.

Frothing should have a similar effect. Amyl alcohol lowers the surface tension of water. Miss Benson removed amyl alcohol on the surface of air globules[25] by raising a froth on, and removing it from aqueous amyl alcohol solution.

It may therefore be deduced from the results of the foregoing experiments that, in petroleum, one or more of the higher hydrocarbons in solution in lower ones, lowers the surface tension of the latter.

## (b) Surface Tension of Petroleum and its Components.

The deduction that higher hydrocarbons should reduce the surface tension of lower ones, when dissolved in them, was confirmed by dissolving varying quantities of paraffin wax in kerosine redistilled between 150°C, and 240°C. and noting the effect on the interfacial tension oil-water.

In the experiments referred to above in which sodium glycocholate was removed at the surface of paraffin oil globules, Lewis employed the drop method for the determination of interfacial tension. As only comparative figures are required for the present purpose the same method was adopted.

For preliminary experiments an ordinary small pipette was fitted on top with a rubber tube and Mohr's clip and had a mark etched on the stem below the bulb. Water was dropped at the rate of 20 drops per minute into kerosine and into the various concentrations of wax in kerosine. The number of drops which fell during the descent of the meniscus from the upper to the lower mark was noted, the rate of flow and temperature being kept as nearly as possible constant for each determination.

The interfacial tension water-kerosine was calculated from the formula,-

$$S = \frac{mg}{\pi a} \left( \frac{d - d'}{d} \right)$$

where S = interfacial tension, d and d' the densities of the heavier and lighter liquids respectively, a = the radius of neck of drop when sides are parallel, m = average weight of one drop in grams, and g the gravity constant. In accordance with Lord Rayleigh's suggestion 3.8 was substituted for $\pi$.

After several weighings of from 5 to 10 drops of water the average weight of one drop was found to be 0.1053 gm.

| | |
|---|---|
| Sp.Gr. of Kerosine | = 0.7952 at 15°C. |
| Neck of drop (average of four readings made by travelling microscope) | = 0.310 mm. |
| Number of drops | (69<br>(69<br>(69 |

. . Interfacial tension = 35.86 dynes per cm.

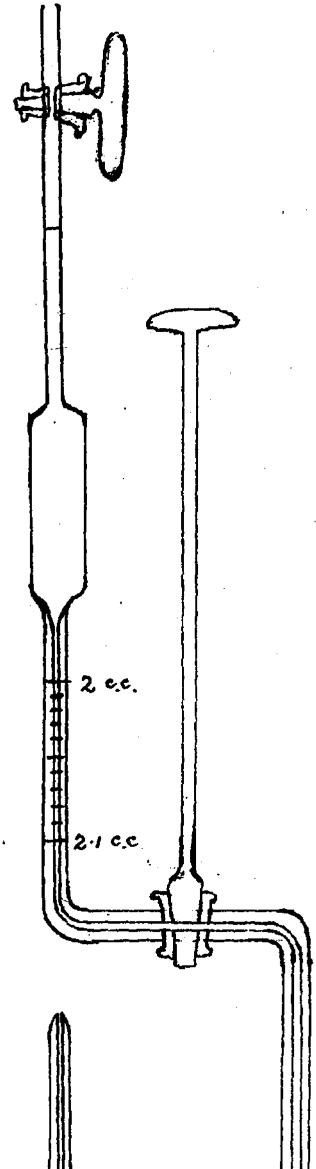
Subsequent determinations were carried out under as nearly as possible the same conditions; the drop number therefore is roughly inversely proportional to the interfacial tension.

| | | |
|---|---|---|
| (Pure) Kerosine | 69.0 | Drop Number |
| 0.1148 % wax in Kerosine | 71.5 | " " |
| 0.2296 % " " " | 73.0 | " " |
| 0.4592 % " " " | 76.0 | " " |

Paraffin wax, therefore, in dilute solution in kerosine, reduces the surface tension of the kerosine by an amount which increases with increasing concentration. Emulsification or frothing of kerosine containing paraffin wax would therefore bring about concentration of wax at the surface layers.

Before this principle can be applied effectively to the removal of components from petroleum a knowledge of the surface tensions of hydrocarbons and their mixtures is essential.

With one or two exceptions, pure hydrocarbons are not readily obtainable in Britain, France or Germany and while preparing these a sample of Hardstoft crude oil was fractionated with moderate steam in order to give fractions of gradually increasing specific gravity. The interfacial tension between each fraction and water was obtained at room temperature and at 3°C. Small quantities of a high fraction were introduced into a lower one and the effect of this addition on the interfacial tension



PIPETTE EMPLOYED FOR SURFACE TENSION DETERMINATION.

was determined, again at room temperature and at 3°C. In the case of fractions, very viscous at room temperature, comparisons were made at a higher temperature.

For the ensuing interfacial tension experiments, a more permanent form of pipette was prepared.

A capillary tube was blown and shaped in the manner sketched. Its capacity was 2.1 cc. and it was graduated in 1/100th. of a cc. from 2.0 cc. - 2.1 cc. The pipette was calibrated by weighing mercury run from it at 15°C. The lower end was turned upwards to permit of the dropping of oil into water and the general design arranged to suit Prof. Boy's[26] method for determining absolute surface tension if need be.

To carry out a determination the pipette was cleaned with alcohol and ether, blown with air, and oil drawn in as far as the upper stop-cock which was then closed. The pipette, filled with oil, was submerged as far as the upper stop-cock, in a cylinder of water at the required temperature, and the whole placed in a constant temperature bath for 15 minutes. The lower stop-cock was then closed and the pipette raised till the graduated part was just above the water level. The upper stop-cock was opened and the lower adjusted to allow oil to drop out at the rate of about 20 drops per minute. When the meniscus reached the graduations,

## Hardstoft crude oil.

Fractionated with moderate steam from fraction 9 onwards. First eight fractions collected together and refractionated:-

* Steam introduced. x At 25°C.

| Fraction | B.P. °C. | Sp.Gr. at 15°C. | Vol. run out. cc. | Drops. | Interfacial tension at 16° C. Dynes per cm. |
|---|---|---|---|---|---|
| 1 | 100-120 | 0.6938 | 2.024 | 44 | 32.29 |
| 2 | 120-140 | 0.7236 | 2.028 | 44 | 30.35 |
| 3 | 140-160 | 0.7348 | 2.022 | 43 | 30.33 |
| 4 | 160-180 | 0.7430 | 2.048 | 42 | 30.78 |
| 5 | 180-190 | 0.7554 | 2.050 | 44 | 28.45 |
| 6 | 190-200 | 0.7612 | 2.040 | 43 | 28.51 |
| 7 | 200-210 | 0.7659 | 2.045 | 42 | 28.24 |
| 8 | 210-220 | 0.7731 | 2.022 | 48 | 24.98 |
| 9 | 220-230 | 0.8127 | 2.050 | 45 | 22.93* |
| 10 | 230-240 | 0.8198 | 2.030 | 41 | 24.18 |
| 11 | 240-250 | 0.8234 | 2.050 | 43 | 23.19 |
| 12 | 250-260 | 0.8277 | 2.034 | 41 | 23.38 |
| 13 | 260-270 | 0.8235x | | | |
| 14 | 270-280 | 0.8315x | | | |
| 15 | 280-290 | 0.8368x | | | |
| 16 | 290-300 | 0.8371x | | | |
| 17 | 300-310 | 0.8402x | | | |
| 18 | 310-320 | 0.8410x | 2.05 | 40 at 25° | 22.44 |

the lower cock was closed and the volume which had passed out noted. For determination above and below room temperature, a jacket containing water at the required temperature was fitted round the stem of the pipette. The results obtained are tabulated on the opposite page.

Francis and Bennett,[27] and Predescu[28] find that surface tension increases with specific gravity. The determination of interfacial tension oil-water, for each of the fractions obtained by the author from Hardstoft crude oil showed a slight but continuous decrease with increasing specific gravity. Fractions boiling above 260°C. were too viscous to be examined at ordinary temperature, but the interfacial tension of the highest fraction, determined at 25°C., was slightly lower than that of the heaviest liquid at room temperature. As increase of temperature alone may have caused this, comparison was left until the effect of temperature had been investigated. Slight discrepancies occur, as for example in fraction 4, which is a little higher than fraction 3. This is not surprising, as we are dealing with mixtures in unknown proportions, and the interfacial tension of a mixture of two hydrocarbons may not be the average of those of the individual components. This was investigated later. A break in continuity will be noticed at fraction 9.

It is interesting to note that it is here that steam was first introduced, and that the first jet of steam may mechanically have carried over some heavy vapour. The first eight fractions were collected as one large fraction and subsequently redistilled. A break in continuity is, therefore, to be expected, yet this break is not by any means so noticeable in specific gravity. Surface tension would, therefore, appear to be a more delicate test of continuity than specific gravity. Quantities of fraction 18 were dissolved in kerosine redistilled between 160°-240°C. so as to obtain solutions varying in concentration from about 0.1 % to about 10 %.

| % of Heavy Oil (Fraction 18) | Sp.Gr.of Mixture | Interfacial at 3°C. | Tension at 18°C. |
|---|---|---|---|
| 0.000 | 0.7867 | 31.91 | 32.11 |
| 0.095 | 0.7867 | - | 30.73 |
| 0.298 | 0.7867 | 31.58 | 30.47 |
| 0.404 | 0.7867 | 30.10 | - |
| 0.513 | 0.7867 | 29.02 | 30.47 |
| 0.834 | 0.7867 | 29.12 | 30.59 |
| 0.907 | 0.7872 | - | 29.89 |
| 1.01 | 0.7874 | 28.39 | (30.10) |
| 2.17 | 0.7881 | (29.18) | 28.96 |
| 3.11 | 0.7886 | 28.17 | 28.42 |
| 4.29 | 0.7952 | 25.87 | 25.81 |
| 9.61 | 0.8008 | (30.31) | 23.38 |

Specific gravities were determined by a Westphal balance. This instrument was not sensitive to the first minute additions of heavy oil, yet the interfacial tension at 3°C. quite appreciably and regularly dropped after these additions up to 4 %. With 9.6 % of heavy oil, viscosity apparently interfered and a higher result was obtained. At 18°C., however, the interfacial tension of an 9.6 % solution was decidedly lower than that of a 4 % solution at the same temperature. In general, within certain limits, the interfacial tension dropped on increasing the concentration at both 3° and 18°, but no general conclusions could be drawn regarding the effect of temperature on the interfacial tensions of individual concentrations. Pure hydrocarbons and known mixtures of these are being investigated for this purpose. That the decrease in interfacial tension with increasing concentration takes place within certain limits only is shown by the determination at 25°C., of the interfacial tension of kerosine alone, fraction 18 alone, and a 9.6 % solution of fraction 18 in kerosine. The figure obtained for fraction 18 is much lower than that for kerosine, yet the 9.6 % solution has an interfacial tension lower than both.

| Interfacial tension | | Dynes per cm. |
|---|---|---|
| Kerosine (Sp.Gr. 0.7867) ----- | water at 25°C. | = 29.09 |
| Fraction 18 (Sp.Gr. 0.8410) --- | " " " | = 22.44 |
| 9.61 % solution of fraction 18 in kerosine (Sp.Gr. 0.8008) --- | " " " | = 20.80 |

In order to effect the separation of fraction 18 from kerosine, on surface layers, the most effective concentration, of those examined, would therefore be 9.6 % at 25°C. A more exhaustive study along these lines, but employing pure hydrocarbons and improved methods for the determination of surface tension, is now being made.

# Part IV.

## (a) Preparation of Paraffins.

## (b) Bromination of Petroleum.

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It was shown in Part III. of this investigation that a partial separation of the components of petroleum without decomposition, could be made by the removal of a froth, or by fractional emulsification. In order to determine the conditions under which the separation of individual components, by these means, could most effectively be made, a study of the surface tensions of hydrocarbons and of their mixtures was necessary.

With the object of preparing pure hydrocarbons of the paraffin series for these determinations a number of experiments were carried out in which accepted methods were employed, but none of those investigated proved suitable for the production of reasonable yields.

The following methods were considered, and while some of them were rejected for reasons stated, others were experimently investigated.

I. Distillation of Petroleum. It has been shown in the introduction to this work, and again, by experiment, in part I, that pure hydrocarbons cannot be prepared from petroleum by distillation.

2. Electrolysis of potassium salts of fatty acids is acknowledged to be inapplicable for the preparation of members higher in the series than propane.

3. Hydrogenation of olefines was omitted as these could not readily be obtained pure.

4. Wurtz' synthesis. Pure monohalides, particularly of higher members are very inaccessible and are probably as difficult to prepare in quantity as the paraffins themselves. The alcohols from which these monohalides may be prepared cannot be obtained in a pure state without great difficulty, principally on account of the proximity of the boiling points of the normal and isomeric forms. The preparation of hexane from propyl iodide was, however, attempted by this method, first benzene being employed as solvent, then ether.

Preparation of Hexane.

300 cc. benzene were dried over calcium chloride, then for 24 hrs. over sodium wire, and removed from the sodium by distillation.

50 cc. propyl-iodide were dried over calcium chloride and distilled; the fraction boiling at 102°- 103°C. being collected. (Isopropyl Iodide boils at 89°C.) 23 gm. propyl iodide were slowly added to 18 gm. benzene and 6.8 gm. sodium wire contained in a round bottomed

flask fitted with a reflux condenser. After standing overnight the benzene solution was decanted off and the residue extracted twice with benzene.

Hexane was removed from the benzene by gentle distillation, the portion boiling below 80°C. being collected.

Benzene which passed over with hexane was removed by repeated freezing at - 10°C. followed by treatment of the liquid residue with 2 cc. oleum. No oil of any kind remained.

The theoretical yield should have been 5.8 gm. hexane, B.P. 69°C.

The method was repeated by allowing 5.8 gm. propyl iodide, 17 gm. sodium, and 43 gm. ether to remain in contact for 48 hrs. in the same apparatus as before.

Subsequent removal of ether by careful distillation left a residue, weighing 0.6 gm., presumably of hexane, but obviously impure.

In both expertments the sodium had formed sodium iodide.

Wurtz' synthesis was not investigated further at this stage as the method is unsuitable for the preparation of hydrocarbons having an odd number of carbon atoms in each molecule. In the preparation of pentane, butane and hexane are produced by the concurrent union of two ethyl and of two propyl radicles respectively. A further disadvantage of the use of alkyl halides for the preparation of paraffins is that the theoretical yield of the pure hydrocarbon is necessarily low because of the high atomic weights of bromine and iodine; the pure alkyl chlorides, being even more difficult to obtain than bromides and iodides, could not be substituted.

## 5. Reduction of Polyhydric Alcohols.

Hydrocarbons may be prepared by the reduction of polyhydric alcohols, of which mannitol is the most easily obtained in a pure state. The alcohol is first converted into the monohalide by hydriodic acid, and the halide into the hydrocarbon by hydrogen from zinc and hydrochloric acid. Many experiments employing recognised methods and recent modifications were carried out. None was very successful, tar formation, during the preparation of the halide being one of the greatest difficulties. The maximum yield of hexyl iodide was about 10 % of the weight of mannitol used. An outline of the methods investigated is given below.

### Preparation of $\beta$-Hexyl Iodide from Mannitol.

Experiment 1.[29] 24 gm. mannitol, 300 cc. hydriodic acid, B.P. 126°C. The mannitol and hydriodic acid were boiled together in a large retort through which a brisk stream of carbon dioxide was passed. The distillate consisted of an oily and an aqueous layer both of which were dark brown in colour. The oily layer after separation and washing, weighed 9 gm. This was distilled with steam and yielded a clear oil distillate weighing 1.4 gm. A brown tarry mass remained in the retort.

Experiment 2.[30] The addition of red phosphorus to the retort has been suggested as a means of preventing reduction in the concentration of the hydriodic acid during the above reaction. This modification was carried out in the manner described by its author, but no increase in the yield was obtained. Once more tar was formed.

Experiment 3. The tarry matter produced in the above experiments may be formed by the decomposition of the hexyl iodide, which is unstable at its boiling point. While purifying hexyl iodide by distillation, the author observed that the compound readily volatilised in steam. Steam was therefore substituted for carbon dioxide and the experiment repeated without, however, increasing the yield. It was then presumed that the tar formation was due to the decomposition of mannitol.

Wxperiment 4. To avoid decomposition of mannitol, the experiment was again modified. 30 gm. mannitol and 300 cc. hydriodic acid were heated on a water bath for 20 mins. The product was distilled under reduced pressure, a slow current of carbon dioxide being passed into the retort during distillation. Under a pressure of 210 mm.Hg. the mixture boiled at 68°C. The $\beta$ -hexyl iodide obtained weighed 2 gm.

Experiment 5. The above experiment was repeated, but in order to increase the yield, the mannitol and hydriodic acid were allowed to react till tar formation commenced. The yield of $\beta$ -hexyl iodide was 1.8 gm.

Experiment 6. The hydriodic acid used in these experiments, with the exception of the first, had been regenerated f from a previous reduction. Experiment 3 was repeated using freshly procured hydriodic acid, The yield ofs hexyl iodide was 2 gm.

Experiment 7. Yellow phosphorus was added in small pieces to 20 gm. of iodine, 20 cc. of water, and 10 gm. of mannitol until the solution was colourless. The mixture was distilled in a current of carbon dioxide, and small pieces of yellow phosphorus added to the distillate until it was colourless. The hexyl iodide after separation weighed about 1 gm.

## Reduction of Alkyl Halides.

In spite of the unsatisfactory nature of the methods a fair quantity of the iodide had accumulated as a result of the experiments. Attempt was made to reduce the hexyl iodide to hexane by the method recommended by Le Bel and Wasserman[31] who say:- "Place the iodide in a hydrogen apparatus containing zinc and hydrochloric acid; the evolved gas passes through a layer of heavy petroleum which dissolves the hexane formed by the reduction".

'Heavy petroleum', being undesirable as a solvent, for reasons which have already been stated in detail, was substituted by a layer of ether. After 3 hours, the ether layer was separated and carefully distilled, leaving a residue of about one drop of hexane.

Perusal of literature pertaining to the production of alkyl halides, and of their reduction to corresponding hydrocarbons, elicited the information that Herzfelder[32.] obtained polybromides by smooth bromination of monobromides, and that he subsequently reduced the polybromides to corresponding hydrocarbons by reduction with hydrogen from zinc and alcohol. From the view point of this research, Herzfelder's work was extremely interesting for he claimed that the smooth bromination of a single monobromide had a definite end-point when just as many bromine atoms had been introduced as the hydrocarbon molecule contained carbon atoms, and that one bromine atom and one only, attached itself to each carbon atom. While his proofs seemed otherwise somewhat inconclusive, the fact that a definite end-point - a single substance

- was reached, was quite clear.

The inefficiency of the methods outlined above for preparing alkyl halides and hydrocarbons had redirected attention to petroleum as a possible starting point.

If petroleum be chlorinated, the resulting mixture may contain several chlorine derivatives of each individual hydrocarbon, and many of these are liquids. To separate them would probably prove as difficult as the separation of a mixture of hydrocarbons. If, however, each paraffin hydrocarbon in petroleum or a fraction thereof can be converted into a single bromo-derivative, it is possible that these may be more easily separated than the mixtures of hydrocarbons.

(b) It has been indicated that the theoretical yield of hydrocarbon obtainable from an alkyl bromide is low because of the high atomic weight of bromine. By reversing the procedure a good yield of alkyl bromide could be expected from a paraffin. Herzfelder states however, that as many bromine atoms may be introduced as the paraffin molecule contains carbon atoms. If applied to petroleum therefore, a high yield of bromo-derivatives could be obtained from even a minute quantity of paraffin present. If separable in a pure state, these bromo derivatives should be sufficiently reactive to permit of conversion into many other substances for the purpose of determining their constitution, Could it be shown that no decomposition had taken place during bromination, it would then be possible to deduce the constitution of the original hydrocarbon components.

Reference to the physical constants of such derivatives as have prepared, and which Herzfelder claims should be produced from each hydrocarbon resulted in the following:-[33.]

| | |
|---|---|
| 1.2.3.-- tribromopropane | m.p. 16°- 17°C. |
| 1.2.3.4.- tetrabromobutane | m.p. 118°- 119°C. (decomposed on boiling) |

1.2.3.4.5.- pentabromopentane, fusible, crystalline plated.

Isomeric pentabromopentanes sublime on heating.

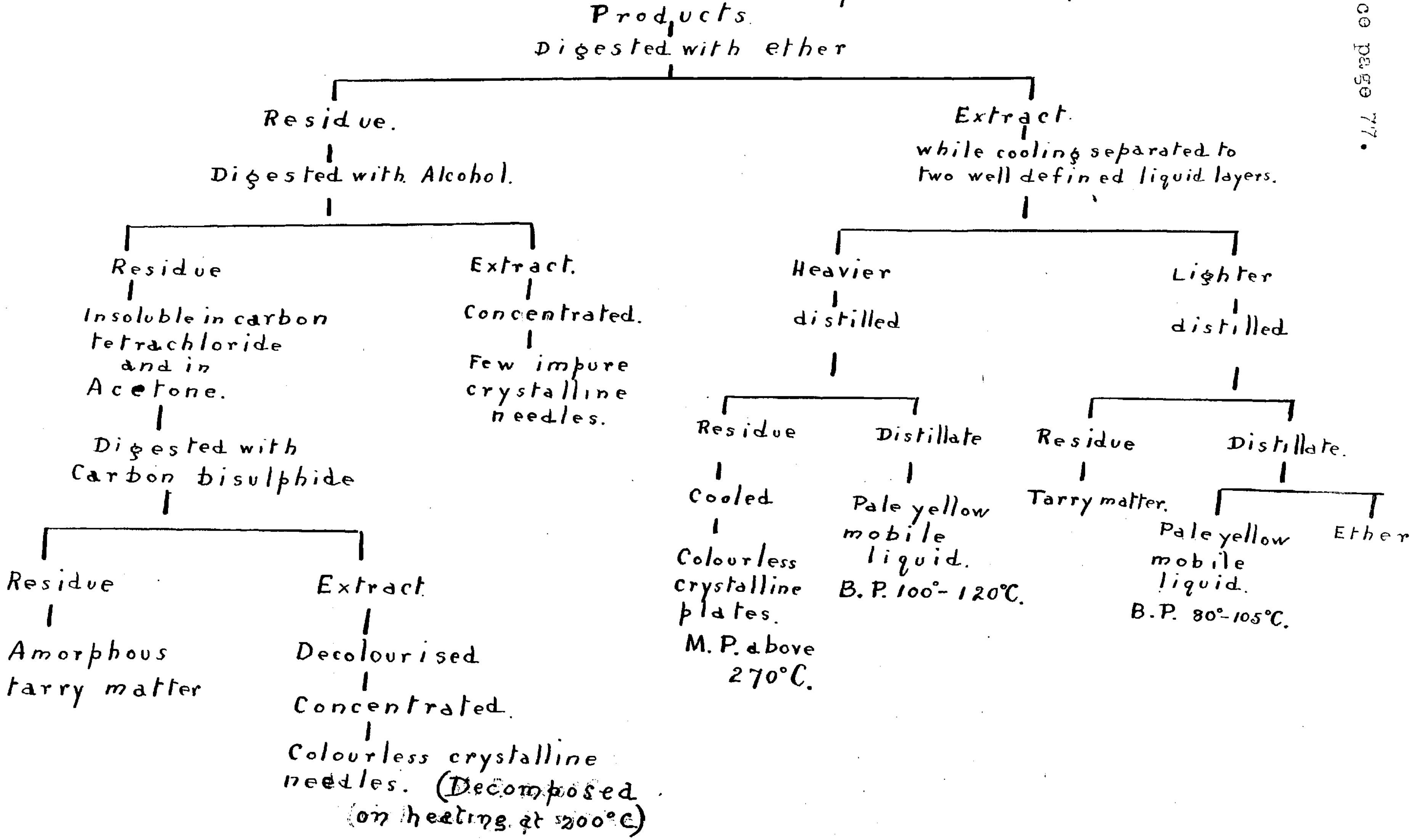
1.2.3.4.5.6.-hexabromohexane, m.p. 152°C., crystalline needles.

The constants of such bromides as are known therefore, and which may be finally produced by smooth bromination, would seem to differ sifficiently to permit of the separation of a mixture of bromo-derivatives.

Crude oil was not employed for bromination in the first instance, but such of the 'light' components as would pass over on warming Anglo-Persian crude oil to 100°C. and passing steam, were removed. This fraction was carefully redistilled without steam, up to 135°C. only, in order as far as possible, to avoid cracking, and smaller fractions collected.

To face page 77.

# Preliminary Bromination.
## Anglo Persian Crude Oil. Fraction B.P. 60°-80°C.
## Outline of method of separation of products.



2,000 cc. Anglo Persian crude oil taken.

Warmed on steam bath, and open steam passed into retort.

498 cc. light oil distillate obtained.

Distillate fractionated without steam and the following fractions collected.

| | | |
|---|---|---|
| B.P. up to 60°C. | 8 cc. | |
| " 60° - 80°C. | 50 cc. | (Hexane B.P. 69°C.) |
| " 80° - 105°C. | 110 cc. | (Heptane B.P. 99°C.) |
| " 105° - 120°C. | 84.5 cc. | |
| " 120° - 135°C. | 86 cc. | (Octane B.P. 125°C.) |
| Residue | 159.5 cc. | |
| Total | 498 cc. | |

## Bromination of Fraction B.P. 60° - 80°C.

A preliminary bromination of those components boiling between 60° and 80°C. was carried out. No unsaturated compounds were present in this fraction; had they been present, their extraction by, say, Edeleanu's method would have been necessary, for an olefine might, by addition and substitution, give rise to the same bromo-derivative as would be obtained from the corresponding paraffin by substitution alone.

Herzfelder's method of bromination was followed, sufficient bromine being weighed out to combine with Hexane, B.P. 69°C. in the following proportion.

$$C_6H_{14} + 6\ Br_2 = C_6H_8Br_6 + 6\ H\ Br$$

34 gm. oil taken. 380 gm. bromine. 5 gm. iron wire.

The iron wire was cleaned and placed along with the oil in a round bottomed flask, fitted with a reflux condenser. The temperature was raised to 60°C. and bromine added drop by drop. After two hours the action had ceased, although bromine was present in excess. The temperature was then raised to 100°C. and with the recommencement of the evolution of hydrobromic acid the addition of bromine was continued. After 189 gm. of bromine had been added tar formation commenced and the addition of bromine was again discontinued. The product was allowed to stand overnight and then extracted with ether.

Endeavour was made to wash a small quantity of the solution in ether with dilute aqueous caustic soda, but an emulsion formed which did not readily separate. The same result followed the substitution of sodium thiosulphate for caustic soda.

The entire product was therefore heated on a steam bath for 30 minutes, to drive off hydrobromic acid and as much bromine as was possible without excessive heating, and subsequently repeatedly extracted with boiling ether. The combined extracts after cooling, separated onto two well defined liquid layers, the lower of which was drawn off.

The upper layer was distilled to remove ether and a pale yellow mobile liquid B.P. 80° - 105°C. remained. This liquid on distillation left a tarry residue which on microscopic examination appeared to be perfectly amouphous.

The lower layer on distillation yielded a pale yellow mobile liquid B.P.100° - 120°C. and a solid residue which after decolourisation with animal charcoal in alcoholic solution, and repeated recrystallisation from alcohol separated as colourless crystalline plates which melted above 270°C.

The insoluble matter which remained after the product obtained by bromination had been extracted by ether was repeatedly extracted with alcohol. On distilling off the alcohol a few impure crystals remained.

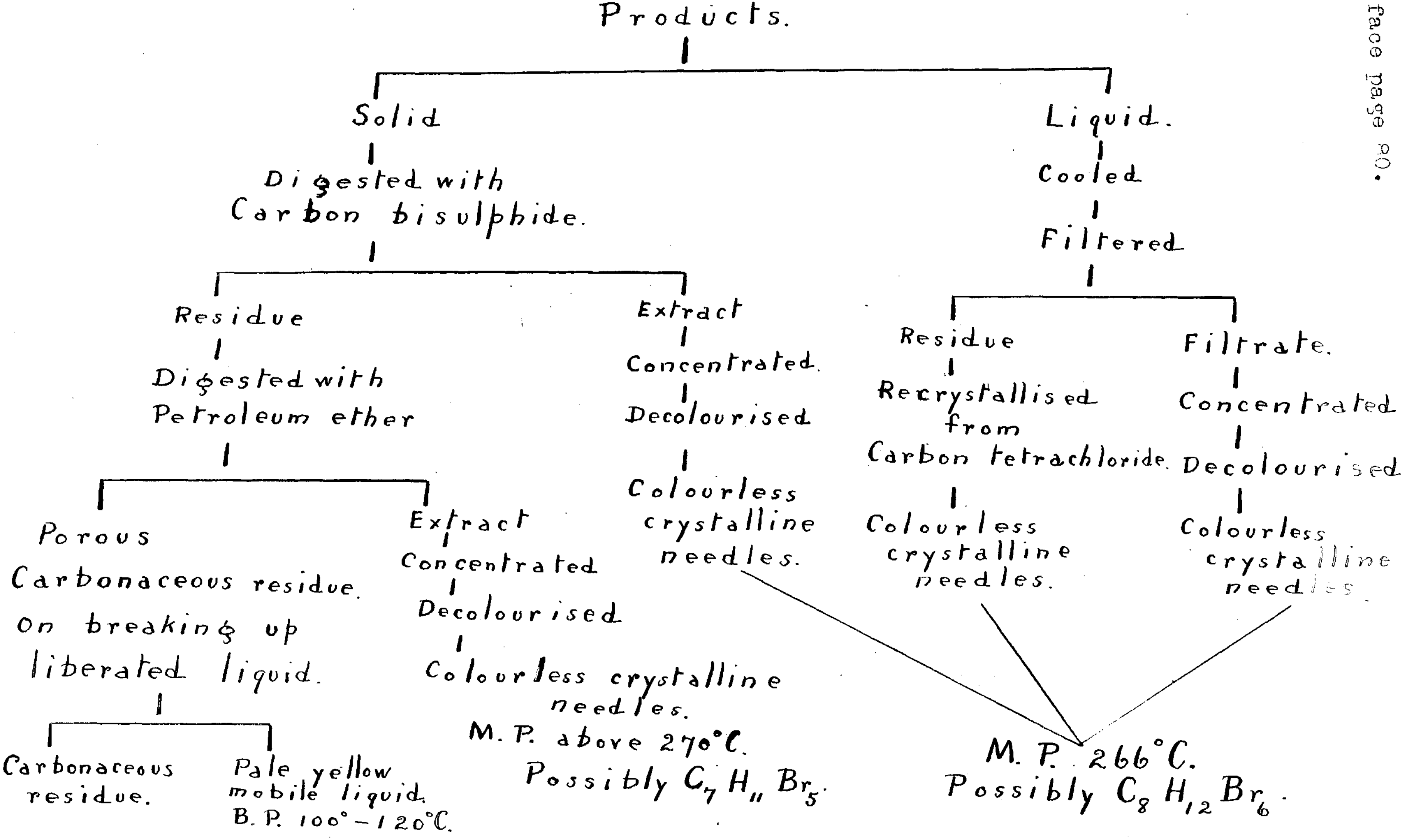
The residue insoluble in ether and in alcohol was examined microscopically and observed to contain a comparatively large quantity of small needle shaped crystals. These were not removed by carbon tetrachloride nor by acetone, but dissolved in carbon bisulphide. From this solution a crop of brown coloured needles was obtained. These were recrystallised from carbon bisulphide after decolourisation by animal charcoal. The colourless needles obtained decomposed

To face page 80.

## Preliminary Bromination.

## Anglo Persian Crude Oil. Fraction B.P. 80°-105°C.

### Outline of method of separation of products.



at 200°C. without melting.

The liquid products obtained in the manner described above, had a pleasant ester-like odour. They contained bromine and on nitration at room temperature, yielded a yellow oil. This, on reduction, yielded an amine which was recognised by the carbylamine reaction.

Preliminary Bromination of Fraction B.P. 80° - 105°C.

100 gm. oil taken. 1,120 gm. bromine.

Bromination was carried out in the same apparatus as was employed for the previous fraction, but, in order to avoid tar formation, no heat was applied. Bromine was added slowly, at intervals, during a period of about three weeks but as the reaction, as indicated by the evolution of hydrobromic acid, was proceeding very slowly, the temperature was raised to 60°C. for one week; at the end of this period however, the evolution of hydrobromic acid once more almost ceased. It was not considered advisable further to raise the temperature without taking precautions to prevent tar formation. The mixture was therefore diluted with carbon bisulphide before heating on a steam bath under a reflux condenser.

A little more iron wire was added at this stage, and rapid evolution of hydrobromic acid temporarily occurred, accompanied by rise in temperature. So far as could be observed the iron completely dissolved in the dark pasty mass. A further addition of iron produced a similar effervescence and rise in temperature, the addition of iron being continued until no more dissolved.

The remaining bromine was added at intervals throughout a period of about two weeks. At the end of this time, a considerable amount of tar had again formed.

The solution of the product in carbon bisulphide was removed by decantation from the solid carbonaceous matter which was subsequently washed with boiling carbon disulphide. After decolourisation with animal charcoal, this solution yielded colourless needle-shaped crystals, which melted at 266°C., and contained 81.38 % Bromine: 2.22 % Hydrogen: and 16.24 % Carbon:

The empirical formula $C_4H_6Br_3$ represents 81.63 % Bromine: 2.04 % Hydrogen; and 16.32 % Carbon.

It is therefore possible that this substance is $C_8H_{12}Br_6$ derived from Octane which boils at 125°C.

The carbonaceous residue after bromination was extracted with boiling petroleum ether, from which a pale yellow liquid B.P. 100° - 120°C. similar to one of those obtained by brominating the petroleum fraction B.P. 60° - 80°C. separated on cooling. Removal of the cold petroleum ether left a solid, which, after recrystallisation, separated as colourless 'needles', melting above 270°C. and containing 80.79 % Bromine, Pentabromoheptane $C_7H_{11}Br_5$ contains 80.81 % Bromine.

Nothing further was obtained from the carbonaceous residue, insoluble in carbon bisulphide and petroleum ehter, by repeated extraction with acetone, chloroform, and carbon tetrachloride respectively. Although prior to extraction with petroleum ether, this substance was a plastic mass, like soft pitch, the removal of the liquid product from it, caused the formation of a porous lump, like petroleum coke, which crumbled to a fine powder after repeated extraction.

The separation of the solid derivatives from the products obtained by brominating both of the above fractions, proved much simpler than was anticipated, a different solvent being required for each.

From the physical constants of the purified polybromides, it would appear, at this stage, that all of the paraffin components have been separated from each other, and from other components.

The liquids may be decomposition products of higher polybromides, or products of the bromination of cyclo-paraffins, which decompose at or below their boiling point, during distillation. Could the tar formation, indicative of decomposition, be prevented during bromination, it would be possible to determine this.

## Prevention of Tar Formation.

The prevention of tar formation would render the final purification of solid products even simpler by rendering decolourisation by animal charcoal unnecessary, and would make a quantitative separation possible.

These preliminary experiments show that in order to achieve this, the petroleum must, during bromination either be diluted with a solvent, inert towards bromine, or the temperature must be kept low. It has been shown that the quantity of halogen carrier recommended for the smooth bromination of an alkyl bromide is insufficient for an equivalent amount of a petroleum fraction.

An excess of iron must be present before bromination will proceed, for after bromination had almost ceased, the addition of iron caused a brisk effervescence, which subsided soon after the iron disappeared, but immediately recommenced on the addition of more iron. The disappearance of the iron indicates the formation of a compound of iron or iron bromide with hydrocarbon. This apparently does not decompose to form a bromo-derivative of the hydrocarbon, unless free iron is present. The addition of iron was made, in these experiments, after vain attempts to speed up the reaction had been made by increasing the temperature. The further rise in temperature caused by the addition of iron in presence of an excess of bromine, undoubtedly contributed greatly towards the formation of the tar. It may be possible, therefore, to prevent decomposition by adding bromine slowly in presence of excess of pure iron at room temperature, and should the reaction show any sign of abatement, to refrain from adding more bromine, or from increasing the temperature, and instead, continuously to add iron in sufficient quantity to cause the bromination again to proceed smoothly, after which, bromine could once more be slowly added.

### Bromination without Decomposition of Products.

34 gm. of fraction B.P. 60° - 80°C. were therefore once more brominated in the presence of 10 gm. instead of 5 gm. of clean iron wire, the bromine being dropped in slowly as before. The temperature of the mixture was never allowed to rise above 16°C. When the action tended to subside, the addition of bromine was stopped, and the end of a spiral of iron wire lowered into the hydrocarbon-bromine mixture. Effervescence immediately recommenced but as the temperature commenced to rise, the wire was partly withdrawn. This produced the necessary diminution in the rate of the reaction, the spiral being gradually lowered as the rate became slower. When the addition of more iron ceased to alter the rate of the reaction, bromine was again dropped into the mixture. In this way it was found possible to add the theoretical amount of bromine in about 20 hours, without any tar fromation whatever, and at a temperature

of from 12° - 16°C.

The bromination was carried out in a draught chamber which was not at any time exposed to direct sunlight, as nitration, and reduction of some of the original petroleum fraction, followed by coupling with $\beta$ - naphthol had produced a red precipitate, indicating the presence of aromatic compounds. The absence of bright sunlight and of high temperature would help to confine the substitution of bromine in aromatic bodies, to the nucleus, and, it was hoped, avoid the formation of more than one derivative from a single hydrocarbon.

Separation of Bromo-derivatives.

The evolution of hydrobromic acid continued for about four days after all of the bromine had been added, and a dark brown plastic mass of products remained. This was repeatedly washed with caustic soda solution, the concentration of which never exceeded normal, so as to avoid decomposition. The products were then washed free from soda by repeated agitation with water. Ether dissolved all of the products except a white crystalline substance, This was filtered off, and was observed to be mottled with minute particles apparently of finely divided iron and carbon. It is possible that such carbon as remained had separated from the iron employed as halogen carrier. Dilute hydrochloric acid removed the iron, and cold carbon bisulphide extracted white needle-shaped crystals, which melted above 270°C. and which contained 80.33 % bromine. As this substance was insoluble in benzene, the determination of its molecular weight was not determined at this stage. White needle-shaped crystals still remained undissolved, and mottled with specks of carbon. These were only very slightly soluble in carbon tetrachloride, absolute alcohol, and petroleum ether respectively.

The removal of ether from the filtrate by a current of air, brought about the separation of two liquids, one superimposed upon the other in well defined layers, and the deposition of white needle-shaped crystals. 8.8 gm. of these crystals were removed by filtration, and, after recrystallisation from ether, they melted at 164°C. They contained 80.05 % bromine, and had a molecular weight 345, indicated by the depression of the freezing point of benzene.

After complete removal of water and ether, in a vacuum desiccator, the liquids were both viscous and light brown in colour. The heavier of the two was apparently stable. No more crystals were deposited after repeated solution in, and removal from it of, ether, nor by fractional precipitation by water from its solution in a mixture of alcohol and ether. This heavier liquid had Sp.Gr. 2.5407 at 15.5°C. On distillation, a pale yellow mobile liquid, which evolved hydrobromic acid at ordinary temperature, passed over at about 70°C. This liquid was similar to those separated from the products of previous bromination experiments. A black tar remained in the distilling flask. A second portion of the heavier liquid was heated to 100°C. under a pressure of 12 mm. mercury. Two drops of pale yellow fuming distillate were obtained, the main bulk of the liquid remaining apparently unchanged. When nitrated, this liquid was converted into a yellow plastic material, which after reduction, and coupling up with $\beta$ - naphthol, yielded a brown precipitate. This dye was fixed on woollen fabric, but its formation was not considered conclusive evidence that the liquid was aromatic.

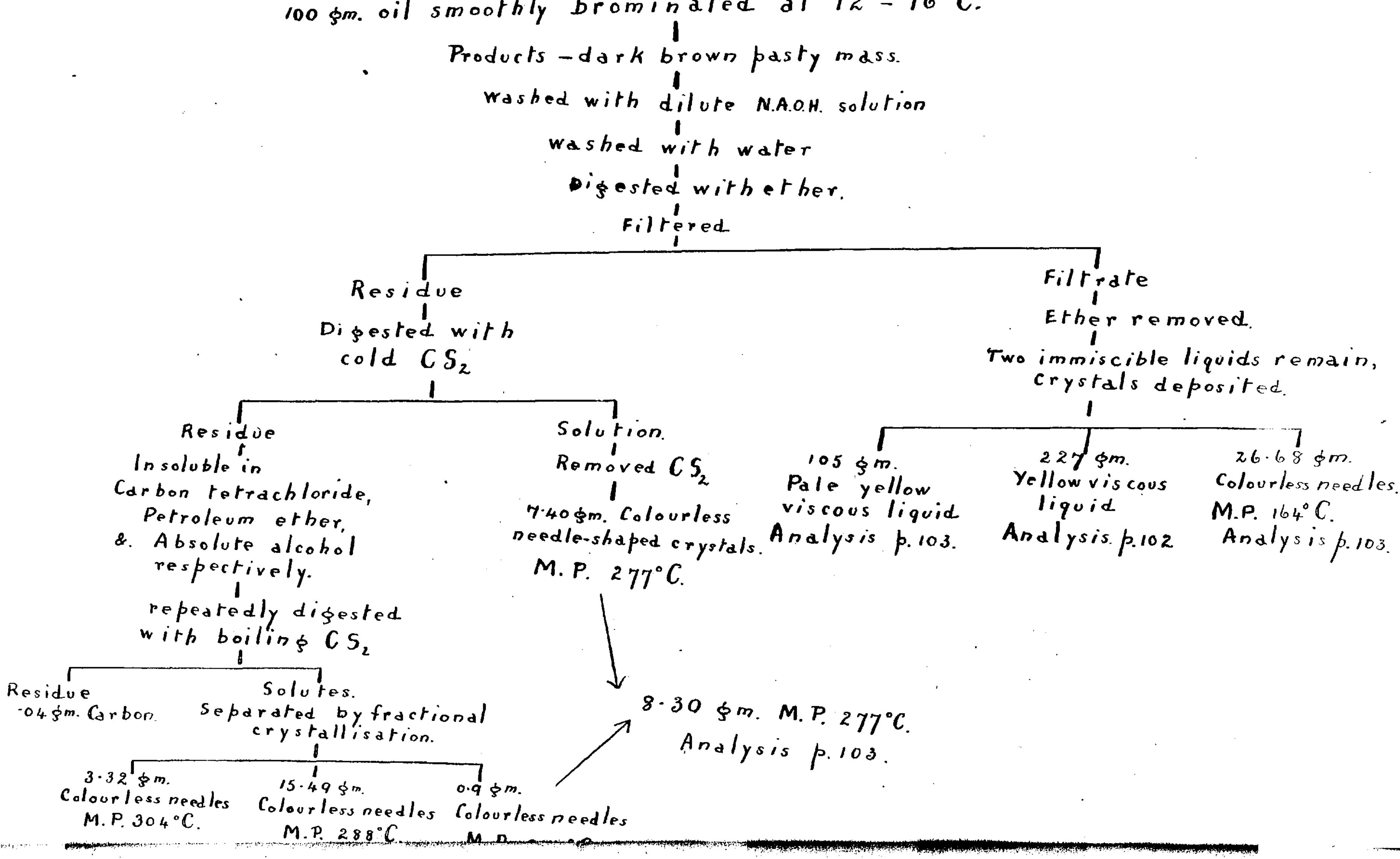
After two days, the colour of the lighter liquid product had changed from pale yellow to brown, and spontaneous evolution of hydrobromic acid had commenced. The liquid was allowed to stand until this action ceased, before any examination of it was made.

It was decided at this stage to prepare a larger quantity of these products, so that their nature might be more closely investigated. Tar formation having been successfully eliminated, a quantitative separation was also aimed at.

# The Separation of the Components of Anglo Persian Petroleum.

## Fraction B.P. 60°-80° C.

## Outline of Quantitative Separation of Components as Bromo-derivatives.



## Quantitative Separation of Components by Bromination.

A fresh supply of Anglo Persian crude oil was obtained, and about 150 gm. fraction B.P. 60° - 80°C. removed from it in the same manner as before.

A small portion of the fraction yielded a red dye after nitration reduction, and coupling up with β - naphthol. This was accepted as an indication of the presence of one or more aromatic compounds.

100 gm. oil were taken. Bromination was carried out exactly as before. The pasty mass was again thoroughly washed with caustic soda, to remove bromine and hydrobromic acid, and with water to remove caustic soda.

As before, a portion of the washed product was insoluble in ether. This was removed by filtration. The removal of ether from the filtrate by a current of air brought about the separation of two liquid layers and the deposition of crystals. On this occasion however, only very few crystals separated. It was presumed that this was due to a slight difference in composition of the original crude oil.

After the liquid products had been separated, from each other, and from solid products, they were again washed with soda and with water to remove last traces of bromine, redissolved in ether, dried over calcium chloride: ether was removed by a current of air, and last traces were drawn from the viscous liquids by allowing them to stand in bell jars under reduced pressure.

## Analyses of Liquid Bromo-derivatives.

The bromine content of each was determined by Carius' method. That of the heavier liquid was 85.17 % : the lighter liquid contained 79.80 % bromine.

Attempt was made to estimate the amounts of carbon and hydrogen in the usual way by combustion, in presence of cupric oxide and oxygen. In each of several experiments the results were low. Those obtained for hydrogen were consistent, but the amount of carbon dioxide obtained varied according to the method of heating, and the temperature at which the combustion was carried out. In every case a carbonaceous deposit was found, "burned into" the glass, near the boat which contained the substance. This deposit was still formed when the substance was intimately mixed with powdered copper oxide before combustion, and remained after heating until the glass became soft. Haas[34.] found that methane did not completely decompose when treated in the usual manner for the estimation of carbon and hydrogen, and suggested the introduction of cuprous chloride, cupric chloride, or lead chloride, but not sodium chloride as a catalyst. Heilbron[35.] was unable completely to decompose cinnamaldehyde semicarbazone by burning with cupric oxide in oxygen, but was successful when lead chromate was substituted for cupric oxide. The latter method proved successful for the combustion of the liquid products obtained in these experiments.

Molecular weights were determined from the amount by which the freezing point of benzene was lowered when the liquids were dissolved in that solvent.

The results obtained were as follows:-

| | Heavier liquid. | Lighter liquid. |
|---|---|---|
| Carbon | 12.74 % | 16.80 % |
| Hydrogen | 1.39 % | 2.38 % |
| Bromine | 85.17 % | 79.80 % |
| Molecular Weight | 480 | 440 |
| Yield from 100 gm. of oil | 227 gm. | 105 gm. |

These figures represent:-

Heavier Liquid.

| | Grams/mol. | Atoms/mol. |
|---|---|---|
| Carbon | 61.1 | 5 |
| Hydrogen | 6.7 | 7 |
| Bromine | 408.8 | 5 |

This substance may therefore be $C_5H_7Br_5$.

Lighter Liquid.

| | Grams/mol. | Atoms/mol. |
|---|---|---|
| Carbon | 73.9 | 6 |
| Hydrogen | 10.5 | 10 |
| Bromine | 351.1 | 4 |

This substance may therefore be $C_6H_{10}Br_4$

The heavier liquid was not appreciably hydrolysed to an alcohol by freshly precipitated lead hydroxide, nor by moist silver oxide.

Analyses of Solid Bromo-derivatives.

That portion of the main product of bromination which was insoluble in ether was digested with cold carbon bisulphide, in which, as in the previous experiment, it partly dissolved.

7.4 gm. white needle-shaped crystals were obtained from the solution. These melted at 277°C., had molecular weight 146, and contained 80.33 % bromine. The cryoscopic method was employed for the determination of molecular weight, as the crystals were insoluble in benzene, chloroform was employed as solvent.

Bromine was estimated by Carius' method.

The determination of the carbon and hydrogen content was carried out in the manner which proved successful for the combustion of the liquid products. Lead chromate did not prove successful in this case. In each experiment a white sublimate formed on the colder part of the combustion tube, at the entrance to the U tube containing calcium chloride.

Endeavour was made to carry out the combustion in a bomb calorimeter, containing pure caustic soda solution, to absorb the carbon dioxide formed. A pellet made from the crystals was supported by a platinum spiral in the calorimeter. Oxygen under 25 atmospheres pressure was introduced, and the spiral raised to a white heat by an electric current. After ten minutes it was found that the pellet had melted and dropped into the caustic soda solution below, without burning. The experiment was repeated, but on this occasion the platinum spiral containing the pellet was supported by the base of a platinum capsule, so that after the pellet melted, the white hot wire would remain in contact with the liquid. After combustion, the pellet had disappeared. but the under surface of the lid of the calorimeter was heavily coated with the white sublimate, formerly found on the colder part of the combustion tube. Preparations were then made to carry out combustion in a tube, six feet long, and filled with lead chromate, and should this be insufficient, to introduce one or other of the various catalysts suggested above.

### Solid Products Insoluble in Ether and in Cold $CS_2$.

Those solids which did not dissolve in ether nor in cold carbon bisulphide, and which were found after a previous bromination to be only slightly soluble in carbon tetrachloride, petroleum ether, and absolute alcohol respectively, were digested with boiling carbon bisulphide under a reflux condenser. By this means 0.85 gm.

needle-shaped crystals were obtained, which, after recrystallisation, melted at 277°C. They were presumed to be identical with those extracted by cold carbon bisulphide, for after mixing with these, the melting point of the mixture remained the same.

A second extraction with boiling carbon bisulphide removed 4.86 gm. colourless needle-shaped crystals, which melted at 288°C.

A third and fourth extraction removed respectively 4.22 gm. and 6.41 gm. colourless 'needles', both of which melted at 288°C., and were identical with the product of the second extraction.

A fifth extraction removed all remaining crystals. After recrystallisation, these melted at 304°C. and were also needle-shaped. The yield was 3.32 gm.

A residue of finely divided carbon remained which weighed 0.04 gm.

It is probable that all of this carbon was obtained from the iron wire added as halogen carrier during bromination. It may therefore be accepted that the separation of components of that portion of Anglo-Persian petroleum which boils between 60° and 80°C. may be carried out without decomposition by smooth bromination, followed by differential solvent action

No attempt has been made at this stage to assign definite formulae to these products, as the experimental error possible in molecular weight and in hydrogen determinations renders it impossible to state definitely whether the substance belongs, for example, to a paraffin, or to a cyclo-paraffin series. In some instances, also, the estimation of carbon by known methods has so far been impossible. As, however, known aromatic and paraffin bromo-derivatives, having percentage composition and molecular weight approaching those of the liquid products here obtained, are solids of high melting point, it is possible that these liquids may not be derived from paraffins as indicated by their analyses, but from members of the cyclo-paraffin series.

# CONCLUSION.

The fractionation of petroleum by methods which do not alter the composition of the components, and the subsequent isolation of individual hydrocarbons from fractions so obtained, have, by this research, now been rendered possible. Much work still remains to be done, however, before every component of a naturally occurring crude oil is isolated, identified and characterised.

The author is at present engaged in the determination of the constitution of those bromo-derivatives, which he has already isolated, and in the reconversion of them into the original hydrocarbon components. After this has been done, the higher fractions of petroleum will be submitted to similar treatment and examination.

The separation of these higher fractions will be effected by the methods suggested in parts II. and III. of this work, there being no other methods at present available for the complete fractionation of petroleum without decomposition.

The principles underlying the methods of fractionation herein employed will undoubtedly displace industrial methods, such as have been examined in part I. Fractional precipitation in its present initial form is quite suitable as a laboratory method, and with the introduction of cheap solvents easily recoverable from the oil and from the precipitant, the industrial application would immediately follow. Fractional emulsification and frothing have been shown by this work to be possible methods for fractionating oil without decomposition. To apply these methods effectively, a knowledge of the surface tensions of pure hydrocarbons and their mixtures is necessary; these are now being determined by the author. As methods of separation depending upon froth flotation are now being applied industrially, and as the principles involved have been proved by this work to be applicable to petroleum, it is probable that this method will find early application.

The comparatively easy and apparently quantitative separation of pure bromo-derivatives of hydrocarbons from crude petroleum, which has been achieved by this work, is a step towards the development of a petroleum chemistry comparable to a certain extent with the chemistry of coal tar. Petroleum contains a multitude of potential raw materials, and the pure bromo-derivatives of these should be useful starting points from which to prepare a vast number of other hydrocarbon derivatives. Apart from their value as research and industrial chemicals, these derivatives will elucidate the structure of those unknown complex molecules which are supposed to exist in the higher fractions of petroleum, and so contribute information which may prove to be of great importance in the domain of chemical theory.

# SUMMARY.

## Part I.

1. Distillation does not separate individual components. The manner in which modification of the modus operandi affects distillates is described. Few components are separated without decomposition, carbon being liberated even in low-temperature continuous stills.

2. Sweating as at present carried out, is inefficient. A successful improvement of Winterstein's process is described.

3. The weaknesses of the more recent, and in some respects more efficient, continuous coolers as compared with the intermittent type are pointed out.

4. The utilisation of vegetable char for decolorising wax is described, and also an apparatus, which at once removes moisture and extracts wax from spent char with boiling solvent.

## Part II.

1. Some components exist in a colloidal condition in crude petroleum, but ordinary methods for coagulating

colloids do not without further treatment effect a separation.

2. Solid paraffin wax can be separated from crude oil by precipitation without previous distillation. The existence of so-called "proto-paraffin" is not necessary to account for the behaviour of solid paraffins in undistilled oil.

3. Crude petroleum may be fractionated by dissolving in a suitable solvent, and adding successive quantities of one or more substances miscible with the solvent, but as nearly as possible immiscible with petroleum.

4. Fractions obtained from Hardstoft "crude" in this way, do not exhibit the same gradation in viscosity as distillates. Higher fractions behave as emulsoids and do not contain a greater percentage of unsaturated components than lower fractions.

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## Part III.

1. Partial emulsification of petroleum reduces the specific gravity of the non-emulsified part, the oil contained in the emulsion having a higher specific gravity than the original petroleum. The removal of a froth from petroleum has a similar effect.

2. As that substance which lowers the surface tension of the solvent to the greatest extent, when in solution

together with other substances, displaces the others from surface layers, an investigation of the surface tension of petroleum and its components was commenced.

3. Paraffin wax, in dilute solution in kerosine, reduces the surface tension of the kerosine by an amount which increases with increasing concentration.

4. The surface tension of fractions of Hardstoft crude oil decreases as the specific gravity increases.

5. The surface tension of a light fraction is lowered by the addition of a heavy fraction, by an amount which, within certain limits, increases with increase in concentration.

6. While the surface tension of a heavy fraction is lower than that of a light fraction, a mixture of these fractions may have a surface tension lower than that of either of the components.

7. When dealing with fractions which are themselves mixtures, no general conclusions can be drawn regarding the effect of temperature on the surface tension of a hydrocarbon.

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## Part IV.

1. Standard methods for the preparation of paraffins do not, in practice, produce satisfactory yields of the pure hydrocarbons.

2. A comparatively easy and apparently quantitative separation of pure hydrocarbon derivatives may be effected by the action of various solvents on the product of smooth bromination of a petroleum fraction.

3. To avoid decomposition during the separation of a higher petroleum fraction for bromination, one of the methods described in parts II. and III. of this work must be employed, as hitherto no method for the complete fractionation of petroleum, without decomposition, has been published.

4. The following constants have been obtained for derivatives extracted from the product of smooth bromination of that portion of Anglo Persian crude oil which boils between 60° and 80°C.

100 gm. oil taken: brominated at 16°C.

<u>Products</u>.

<u>Yellow viscous liquid</u>.

Sp.Gr. 2.5407 (water = 1) at 15.5°C.

Mol.Wt. 480

Bromine 85.17 % Yield, 227 gm.

Carbon 12.74 % Decomposes with evolution of HBr.

Hydrogen 1.39 % and deposition of tar at 70°C.

These figures correspond with the formula $C_5H_7Br_5$

Pale yellow viscous liquid.

Mol.Wt. 440.20

Yield, 105 gm.

Bromine 79.80 %

Carbon 16.80 %

Hydrogen 2.38 %

Spontaneously decomposes with evolution of HBr. on standing at ordinary temperature.

These figures correspond with the formula $C_6H_{10}Br_4$

Colourless crystalline"needles".

M.P. 164°C.

Bromine 80.05 %

Yield, 26.68 gm.

Mol.Wt. 355

Colourless crystalline "needles".

M.P. 277°C.

Bromine 80.33 %

Yield, 8.30 gm.

Mol.Wt. 146

Colourless crystalline "needles".

M.P. 288°C.

Yield, 15.49 gm.

Colourless crystalline "needles".

M.P. 304°C.

Yield, 3.32 gm.

Carbon (presumably from iron employed as halogen'carrier')

0.04 gm.

5. Other substances were obtained from preliminary bromination experiments, but as decomposition was indicated by the deposition of tar during these brominations, and as the substances were not produced when bromination was

effected without tar formation, it was presumed that the substances were decomposition products. Their analyses are given in the description of preliminary bromination experiments.

6. Bromination can only be carried out in the presence of an excess of iron.

7. Decomposition occurs when bromination is allowed to proceed too vigorously, or above room temperature. No decomposition took place during smooth bromination at from 12° - 16°C.

8. Carbon and hydrogen cannot be estimated in the products, by combustion in the ordinary way. The substitution of lead chromate for cupric oxide renders their estimation possible in some of the derivatives, but not in others.

9. The products were easily separated from each other, although members of the paraffin, aromatic, and possibly cyclo-paraffin series, were present in the original crude oil.

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