CLASSIFICATION OF CRUDE OILS.

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Introduction.

Several attempts to classify crude oils are recorded in the literature,[16] but only the more recent developments will be described in this review.

The accuracy and completeness of the classifications depend on our knowledge of the individual compounds or groups of compounds in the petroleum and on the accuracy of methods to detect and determine them.

Some references have been selected to show the progress made during recent years.

As to the determination of groups of compounds, besides referring the reader to the methods of various Standardization Committees, a few references may be quoted.[1]

For the purpose of identification of the compounds themselves the crude oils have first to be separated into fractions.   A system [10] for this fractionation, which makes use of distillation, extraction, crystallization, and adsorption, has been chiefly developed by A.P.I. Research Project 6.

Of the many physico-chemical properties of the compounds, especially in the petroleum fractions, electromagnetic spectra [12, 13, 14, 15] are very helpful in throwing light on the question.

In connection with names of compounds [8] present in petroleum and its products, attention is directed to a review by Trusty,[9] and also to some [2] [3, 4, 5, 6, 7] of the many research papers of the above-mentioned A.P.I. Research Project 6.

Historical Review.

The earlier classifications consider geological distribution,[16a, b] chemical composition [16a, b, c, d, e, f, k, l, m] or physical properties (e.g., optical activity,[16h] solubility [16i, j]).

Recent Classifications.

(A) *U.S. Bureau of Mines Classifications.—Methods to Evaluate the " Base."*

The Bureau of Mines of the United States has published reports on crude oils classifications, which distinguish various " bases."

In 1927, N. A. C. Smith [17] differentiated four " base "-groups (see Table I.[18]) and in a Bulletin published later [19] the usefulness of this system is also tested.

With the progress of the science of petroleum it was found that the number of groups was not sufficient : three of the four classes were retained and four intermediate groups were added [20] (see Table II.).   The last two classes are possible according to this classification, but no examples of either of them have been found among the many hundred samples analysed by the Bureau of Mines (at least until 1939).[21]   It may be mentioned that according to Lane and Garton,[22] about 85 per cent. of 800 analysed crude

B

TABLE I (1927).

Base.	Gravity of Key Fraction No. 1.*		Pour Point of Key Fraction No. 2,† °F.	Viscosity of Lubricating Distillates.
	° A.P.I., 60° F.	Spec. gr., 60°/60° F.		
Paraffin	40·0° or lighter	0·8251 or lighter	Above 5°	Low
Intermediate	33·1° to 39·9°	0·8597 to 0·8256	Above 5°	Medium
Hybrid	33·0° or heavier	0·8602 or heavier	Above 5°	Fairly high
Naphthene	33·0° or heavier	0·8602 or heavier	Below 5°	Very high

TABLE II (1935).

Base.	Light Fraction.	Heavy Fraction.	Gravity of Key Fraction No. 1.*		Gravity of Key Fraction No. 2.†	
			° A.P.I., 60° F.	Spec. gr., 60°/60° F.	° A.P.I., 60° F.	Spec. gr., 60°/60° F.
Paraffin	Paraffinic	Paraffinic	40·0° or lighter	0·8251 or lighter	30·0° or lighter	0·8762 or lighter
Paraffin–Intermediate	Paraffinic	Intermediate	40·0° or lighter	0·8251 or lighter	20·1° to 29·9°	0·9334 to 0·8767
Intermediate–Paraffin	Intermediate	Paraffinic	33·1° to 39·9°	0·8597 to 0·8256	30·0° or lighter	0·8762 or lighter
Intermediate	Intermediate	Intermediate	33·1° to 39·9°	0·8597 to 0·8256	20·1° to 29·9°	0·9334 to 0·8767
Intermediate–Naphthene	Intermediate	Naphthenic	33·1° to 39·9°	0·8597 to 0·8256	20·0° or heavier	0·9340 or heavier
Naphthene–Intermediate	Naphthenic	Intermediate	33·0° or heavier	0·8602 or heavier	20·1° to 29·9°	0·9334 to 0·8767
Naphthene	Naphthenic	Naphthenic	33·0° or heavier	0·8602 or heavier	20·0° or heavier	0·9340 or heavier
Paraffin–Naphthene	Paraffinic	Naphthenic	40·0° or lighter	0·8251 or lighter	20·0° or heavier	0·9340 or heavier
Naphthene–Paraffin	Naphthenic	Paraffinic	33·0° or heavier	0·8602 or heavier	30·0° or lighter	0·8762 or lighter

* Fraction 250–275° C. (482–527° F.) at atmospheric pressure, Bureau of Mines Hempel method.
† Fraction 275–300° C. (527–572° F.) at 40 mm. absolute pressure, Bureau of Mines Hempel method.

oils from the producing fields throughout the world fell definitely in one of the three classes : paraffin, intermediate, or naphthene base.

Nelson [23] gives a list of methods for judging the base of an oil. Apart from considering the properties indicated in the reports by N. A. C. Smith,[17] and Lane and Garton,[20] there are several methods which make use of the fact that properties are a function of the character of crude oils for the purpose of evaluating the " base " of stocks.

One can compare the properties of an unknown oil with the properties of known stocks. This method, however, has to be applied to a large number of samples.[24]

The " cast " of lubricating oils gives to a certain extent information on the base.[25]

The gasoline content plotted against specific gravity of crude oils shows zones for the three main bases of oils.[26]

Some of the many [27] methods which correlate two or more physical properties in order to obtain an " average " chemical constitution or the " predominating " constituents in petroleum fractions are the viscosity index, the characterization factor, the characterization gravity, and, quite recently, the correlation index.

The viscosity index and the viscosity gravity constant have been extensively described in the literature,[28] and only reference to this literature need be made here.

The characterization factor has been developed by members of the staff of the Universal Oil Products Company,[29, 30, 31] and is defined as the ratio of the cube root of the average boiling point (in degrees Rankine) to the specific gravity at $60°/60°$ F. For highly paraffinic crudes this factor is 12·5–13·0, while for aromatic or naphthenic crude-oil fractions its value is 10 or below, and the increase between 10 and 12 indicates the increase in paraffinicity. The factor has also been related to many other physico-chemical properties.[30] It is additive on a weight basis.[32]

The Standard Oil Company of California has developed a test to classify heavy oils as to their paraffinicity, the characterization gravity,[33] which is defined as " the arithmetic average of the instantaneous gravities of the distillate boiling at $350°$, $450°$, and $550°$ F. vapour-line temperature at 25 mm. pressure in a true-boiling-point distillation."

H. M. Smith [34] states that his correlation index

" cannot be compared to a ' base ' system of classification as it is not a means of grouping crude oils according to their properties. It provides a cross-sectional view of the distillable portion of a crude oil, employing for this purpose numbers or indexes that represent the average boiling-point and specific-gravity characteristics of the distilled fractions."

This method of correlation of physical properties is therefore not meant to evaluate the " base " for the " base " system, and the system of correlation indexes can with advantage be included in analyses [39] as a classification on its own or in addition to the " base " system.

Smith [34] claims, that

" the defects of the ' base ' system are eliminated ; Differences are shown equally with similarities, there are no border-line cases or

doubtful classifications, and names are not used, hence the danger of forming misconceptions due to the name is eliminated."

It will perhaps be interesting to give a short description of the development and use of this term.[34]

Smith considers first the relationships between boiling points and specific gravities existing in 1940 : the boiling point–gravity constant of Jackson [35] for crude-oil fractions and the characterization factor [29] for pure hydrocarbons. He reaches the conclusion that an ideal relationship between boiling point and specific gravity should show systematic differences between the members of the homologous series of hydrocarbons and also between the homologous series. This ideal case is not entirely reached, but the reciprocals of the boiling points, in degrees Kelvin, for the normal paraffins plotted against their specific gravities (at 60° F.) " G " show a linear relation. This line is used as a reference base for the interpretation of the other hydrocarbons and, because no hydrocarbon of any other series with the same boiling point has a lighter specific gravity, this limiting boundary has been assigned an index number C.I. of O. A line parallel to it and passing through the co-ordinates of the hydrocarbon benzene has been given an index number C.I. = 100. These two lines enclose an area which contains most of the hydrocarbons, except polynuclear components.

The equation for the straight lines is : $\dfrac{1}{°K} = b - 9{\cdot}7396 \times 10^{-3}\ G$, where

b is the intercept on the $\dfrac{1}{°K}$ axis. b for the line through the normal paraffins is $9{\cdot}392 \times 10^{-3}$, b for the line through benzene is $11{\cdot}448 \times 10^{-3}$. The correlation index equation is :

$$\text{C.I.} = \frac{48{,}640}{K} + 473{\cdot}7\ G - 456{\cdot}8.$$

This equation may be applied to pure hydrocarbons, and also to fractions of crude oils, in which latter case C.I. is only an average value for the hydrocarbon mixtures. According to Smith, fractions with C.I. 0–15 are almost certainly predominatingly paraffinic ; a C.I. above 50 indicates " that aromatic rings probably predominate," and a C.I. 15–50 indicates " naphthenes or different mixtures of paraffins, naphthenes and aromatics." Side-chains have an influence on the value.[36] When applied to crude oil fractions, the " average boiling point " " K " is used. There are several definitions for this term.[31] All can be obtained from the volumetric average boiling point by applying a correction factor based on the slope of the distillation curve. For small values of the slope the correction is smaller than the errors of the distillation method, and the volumetric average boiling point can be used with an accuracy of within one index number.[34] The volumetric average boiling point is determined by measuring with a planimeter the average height of the curve from the temperature axis, or by averaging the temperatures for the initial point, end point, and temperatures of each 10 per cent. of the distillation. Smith [37] gives two tables by means of which one can read the correlation index for any given specific gravity of the Hempel fractions. The correlation index is not additive.[40] It seems useful in obtaining refining characteristics of crude

oils (see also under " Decimal System "), which subject Smith [38] discusses in a Report on Illinois crude oils, in which he proves that oils which had been shown to have a similar correlation index had been used by refiners to manufacture a similar series of products.

In another Report on Illinois crude oils, Rees, Henline, and Bell [39] give the correlation indexes and characterization factors for each fraction of their numerous Hempel Method Distillations.

(B) *Decimal System.*

A decimal system has been proposed by Voinov,[41] and is being further developed. Voinov classifies the crude oils into classes, sub-classes, and groups, according to their properties, and so far has assigned 3-figure numbers. The figures in the numbers so far consider the content of resinous substances, sulphur, and paraffins.

Two motives underlie the work to develop methods for analysing, characterizing, and classifying crude oils; the one is the purely scientific purpose of furthering the progress of our knowledge, the other is the wish to obtain characteristics of crude oils which are of use to the refiner in selecting suitable crudes for manufacturing desired products.[42, 43, 44]

Whatever classification of crude oils has been adopted, based on either separate or combined application of schemes with regard to geographical distribution, geological location, physical properties, chemical properties, chemical composition, products, etc., numbers can be assigned to each item of the adopted classification by applying the decimal classification of L. C. Uren [45]—which is a modification of Dewey's system—and/or the Bruxelles System [46, 47].

(C) *Classification with Regard to Products.*

A short explanation of what is meant by classification " with regard to products " : Beiswenger [43] differentiates twelve types of crudes (" A " to " L "), and shows the differences in yield and quality of various fractions. Theoretically one can nowadays produce any type of refined product from any crude oil; however, the selection of the refiner will be influenced [43] by

    1. Processing cost.
    2. Yield of products of desired characteristics.
    3. Processing equipment available to him.
    4. Price of products.

Although such a system will probably be very fluctuating, being a function of extremely variable factors, it seems [47] worthy of further development.

CONCLUSION.

Having quoted a few selected references on the present state of our knowledge of the composition and properties of crude oils, some older classifications [16] have been named and various more recent systems briefly reviewed.

The more recent systems are the classifications by N. A. C. Smith [17] and Lane and Garton,[20] who distinguish groups of " bases " ; the system by H. M. Smith,[34] who introduces the correlation index ; the scheme by Voinov,[41]

who applies a decimal system; and the arrangement by Beiswenger,[43] who classifies crude oils according to their products.

Further, the essential features of several methods have been mentioned, which enable one to evaluate the " base " (Table I., Table II.,[24, 25, 26, 28, 29, 30, 33]).

Literature which refers to geographical distribution and geological location, or which relates to the problem of origin of crude oils (*e.g.*, classifies the petroleum as carbonaceous mineral [48]) has not been dealt with.

Already to-day many organic compounds can be directly separated from crude oils by fractionation methods [10] or synthesized from them by applying various processes [43, 44]. It will be interesting to see whether, and if so how, (1) the progress of our knowledge of the compounds present in the crude oils of the world, (2) the progress in synthesizing new products from petroleum as the ultimate raw material, will influence the development of classifications. If the classifications tend to become more extended and/or subdivided, it is possible that, as outlined above,[47] any adopted classification of crude oils will get assigned numbers to its items, in order to aid the refiner in choosing quickly the appropriate crude oil for his production.

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THE MICROBIOLOGICAL ASPECTS OF GASOLINE INHIBITORS.

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Gasolines are stabilized against gum and colour formation, and the precipitation of TEL, by the addition of suitable substances known as inhibitors or anti-oxidants. The use of anti-oxidants to inhibit the autoxidation of organic compounds was reported by Moureu and Dufraisse in a series of over thirty publications starting in 1922.[1] The stabilization of motor fuels by the addition of inhibitors was first introduced in England in 1926, where tricresol was employed in motor benzoles.[2] Three years later the first use of inhibitors by the petroleum industry was reported in papers by Egloff, Faragher, and Morrell.[3] Since that time gasoline inhibitors have become regularly employed in stabilizing essentially all gasoline motor fuels.

The chemical mechanism by which the usual inhibitor concentrations of about 0·002 per cent. by weight can successfully stabilize gasolines during storage periods of up to eighteen months has never been adequately explained. It is known that the formation of gum is represented by a chain of chemical reactions, and that inhibiting or preventing any reaction in the chain will consequently retard or prevent the production of gum as the final product. Hydrocarbon peroxides are known to represent the first step in the formation of gum in gasolines. Gasoline inhibitors apparently exert their effect by preventing this initial peroxidation. This contention is supported by the fact that peroxide concentrations are usually negligible in inhibited gasolines stored in the dark.

Gasoline inhibitors are sometimes referred to as "anti-oxidants." Anti-oxidants are generally assumed to protect the substance to which they are added by the preferential oxidation of the anti-oxidant molecules. The period of protection, or "induction period," continues until the anti-oxidant is completely oxidized. This concept requires that one molecule of anti-oxidant be destroyed for each reaction chain which is broken or prevented from starting. The number of oxidation chains which are initiated in the absence of an anti-oxidant even during short periods of storage far exceeds the number of molecules of inhibitor which are present. This phenomenon is usually explained by following the original concept of Moureu and Dufraisse.[1] These workers postulated that the oxidized anti-oxidant molecule breaks down to yield inactive oxygen plus the original anti-oxidant molecule which is ready to de-activate another activated oxygen molecule. Milas[4] points out that a mechanism of this kind is thermodynamically unsound, since no provision is made for the energy which must be liberated by the breakdown of the oxidized anti-oxidant molecule.

Recent studies in these laboratories[5] have shown conclusively that

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various micro-organisms in the water phase which is normally present below gasoline motor fuels in storage may have a pronounced deteriorating effect on the motor fuel. This effect has also been produced by certain gasoline-soluble bacterial extracts. The bacterial activity was found to result in many cases in the greatly increased formation of peroxides and gum in motor gasolines and the precipitation of lead tetraethyl from aviation gasolines. In a few cases the results of bacterial action were found to be actually beneficial to gasoline stability. This study has also shown that all the compounds which are employed commercially as gasoline inhibitors contain a phenolic, or polyphenolic group, and thereby possess antibacterial properties. A number of organic dyes also are known to be reasonably good gasoline inhibitors. The bacteriostatic properties of such compounds is well known.[6, 6a] An incomplete list of some of the better inhibitors and reference to the bactericidal powers of the inhibitors, or very closely related compounds, is shown below.

TABLE I.

Literature References which Describe the Bactericidal Properties of Several Common Gasoline Inhibitors.

Compound.	Induction Period.[3]	Described as Inhibitor by—	Described as Bactericide by—
a-Naphthol	2250	Fischer and Gustafson [7]	Raiziss and Clemence [8]
p-Aminophenols	2340	Rogers and Voorhees [9]	Ostromislensky [10]
Hydroquinone	85	Lewis and Mead [11]	Maeda [12]
o-, m-, p-Cresols	210	Hoffert and Somerville [2]	Kanoa [13]
Pyrogallol	2185	Lewis and Mead [11]	Maeda [12]
Catechol	2400	Hyman and Ayres [14]	Maeda [12]
b-Naphthol	330	Pure Oil Co.[15]	Raiziss and Clemence [8]
Guaiacol	105	Egloff, et al.[3]	Read [16]

This relationship between the common gasoline inhibitors and their disinfectant properties, together with the fact that bacteria are found to exert a particularly detrimental effect upon gasolines during storage over water, suggests that an important function of these inhibitors is their ability to minimize bacterial action. Since the bacteria live in the water phase and use the gasoline as their carbon source, it is logical to assume that the bacteria tend to congregate on the water side of the gasoline–water interface. The important characteristics of a satisfactory gasoline inhibitor are that the substance is soluble in gasoline and as nearly insoluble in water as possible. To be effective as disinfectants against micro-organisms below the gasoline–water interface, it is necessary that the bactericidal group in the chemical structure of the disinfectant be located in the water phase. It is evident that the common gasoline inhibitors which are used commercially depend on their phenolic groups for their bactericidal properties. It is also known that phenol and other aromatics which possess a highly polar radical have a strong tendency to orient themselves at the interface between a non-polar organic solvent and water, so that the polar radical is located in the water phase and the benzene ring is in the organic solvent. In this way a gasoline inhibitor which contains a phenolic group would orient itself at the interface in such a

way that the toxic hydroxyl group is located below the interface in the proximity of the bacteria.

The efficiency of gasoline inhibitors as bactericides will depend on their concentration at the gasoline–water interface. No direct measurement of this concentration was possible. Gibbs' rule states that if the interfacial tension of a solvent is reduced by increasing the concentration of the solute, then the solute will be concentrated at that interface. Thus a decrease in interfacial tension at the gasoline–water interface when an inhibitor is added would indicate that the inhibitor is concentrated on the gasoline side of the interface. The following surface and interfacial tension data were obtained on an unleaded aviation gasoline base stock with several commercial gasoline inhibitors and lecithin, which is added to gasolines to increase inhibitor efficiency. The concentration of the inhibitors was approximately 0·0012 per cent. by weight and of the lecithin, 0·005 per cent. by weight. These interfacial tension measurements were made with a ring type tensimeter.

TABLE II.

Surface and Interfacial Tension Relationships of an Inhibited Aviation Gasoline Base Stock.

System.	Interfacial Tension.	
Gasoline–air	28·0 dynes/cm.^{2}	
Gasoline + lecithin–air	27·9	,,
Gasoline + *N*-*n*-butyl-*p*-aminophenol–air . . .	27·9	,,
Gasoline + 2 : 6-di-*tert.*-butyl-4-methyl phenol–air . .	27·9	,,
Gasoline–water	36·0	,,
Gasoline + lecithin–water	nil	,,
Gasoline + *N*-*p*-butyl-*p*-aminophenol–water . .	20·8	,,
Gasoline + 2 : 6-di-*tert.*-butyl-4-methyl phenol–water .	33·8	,,
Gasoline + *N*-*iso*butyl-*p*-aminophenol–water . .	18·0	,,
Gasoline + *N*-*n*-butyl-*p*-aminophenol + lecithin–water .	1·5	,,

There is no question that the inhibitors and lecithin are strongly adsorbed at the gasoline–water interface. Thus, according to Gibbs' rule, these materials will be concentrated at the interface. The orientation concept then provides that the phenolic hydroxyl group will be located in the water phase at the interface where the bacteria are also thought to concentrate to gain easy access to the gasoline hydrocarbons.

Fig. 1 shows the orientation of several inhibitor molecules at the gasoline–water interface. It would be expected that compounds such as catechol with two phenolic hydroxyl groups which can both be located in the water phase at the same time would be more effective than the monohydroxy phenols. It is apparent that the *p*-aminophenol type of inhibitor which is used so widely in the industry consists essentially of a phenolic group, which is oriented with the toxic hydroxyl group in the water phase and great enough mass of hydrocarbon radicals to make the molecule more soluble in gasoline than in water. Thus *p*-cresol is a better inhibitor than phenol, because phenol is too soluble in water and does not tend to concentrate at the gasoline–water interface so readily. The cresols generally are also known to be more toxic than phenol, as their high

phenol coefficients indicate. Usually these hydrocarbon groups are tied to the phenol by means of an amino-nitrogen atom. The alkylated phenols, especially those which may occur naturally in the crude, are also known to make excellent inhibitors. It is easily observed from the illustration that hydrocarbon groups which are substituted in the *para* position to the phenolic hydroxyl group are the most effective in maintaining the desired orientation of the hydroxyl group in the water phase.
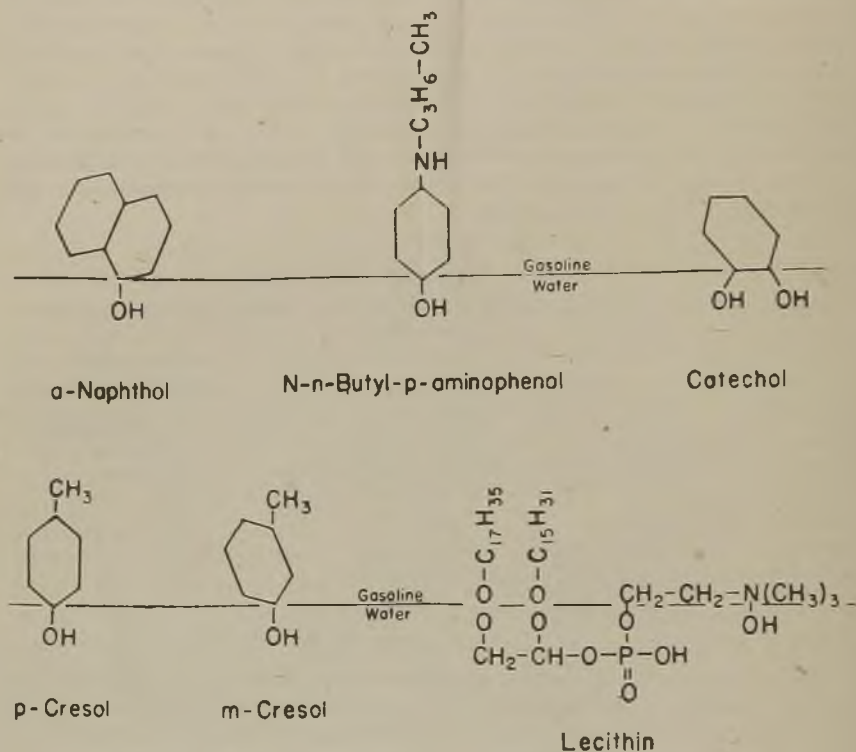

FIG. 1.

THE ORIENTATION OF INHIBITOR MOLECULES AT THE GASOLINE–WATER INTERFACE.

Substitution in the *ortho* and *meta* positions should not be so effective in this respect, since they would exert a moment on the benzene ring which would tend to pull the phenolic hydroxyl group from the water phase. Two hydroxyl groups on the same benzene ring are advantageous if they are *ortho* to one another so that they can both be located in the water phase at the same time. More than one hydroxyl group located in the *meta* or *para* positions is a disadvantage, since the benzene ring must lie in the interface, thereby reducing the effectiveness of the hydroxyl groups.

The *p*-aminophenol compounds which are used so extensively as gasoline inhibitors in the industry are secondary amines, and should serve as effective reducing agents capable of decomposing hydrocarbon peroxides. Thus, in addition to the toxic phenolic group, these compounds also con-

tain a reactive group which may destroy such hydrocarbon peroxides as are formed.   Fig. 1 shows that this amino group is oriented in the gasoline phase somewhat above the gasoline–water interface.   In this location it is available to reduce any peroxides which may diffuse from the interface towards the main body of the gasoline.   It appears that a gasoline inhibitor like N-n-butyl-p-aminophenol serves in the dual rôle of (1) inhibiting bacterial peroxidation by the toxic phenolic group and (2) reducing peroxidized hydrocarbons by the oxidation of the amino group.

According to this concept of inhibitor action, a particularly effective inhibitor for the storage of gasoline over water might be a substituted catechol such as 1 : 2-dihydroxy-4 : 5-di-N-alkyl aminobenzene, which would be insoluble in water and be capable of orientation with two toxic phenolic hydroxyl groups below the gasoline–water interface.

Lecithin as an Inhibitor Intensifier.

The use of soybean lecithin has been described in the literature to increase inhibitor efficiency.[17, 18, 19]   The mechanisms by which this is accomplished are vaguely asserted to be " both physical and chemical." [17] It has also been suggested that lecithin acts as a peptizing agent or as a protective colloid in preventing the formation of haze in leaded gasolines.[19] Lecithin is found to be insoluble in water and soluble in gasoline in what appears to be a true solution.   Since the choline and oleic, palmitic and glyceryl phosphoric acid which are the apparent reactive components of lecithin did not give the same stabilizing effect as lecithin itself,[17] it is concluded that it is the physical size of the non-polar molecule which accounts for this property.   The fact that lecithin is so strongly adsorbed at the gasoline–water interface suggests that its actual function in increasing inhibitor efficiency when gasoline is stored over water may be an ability to facilitate the orientation of the phenolic inhibitors at the interface. Previous work in these laboratories has shown that the rate of gum formation in gasolines stored over water is greatly increased by the presence of air or oxygen in the water phase.[20]   It was also concluded from the same work that most of the deterioration takes place at the gasoline–water interface.

Two possible explanations of the mechanism by which lecithin is capable of inhibiting the deterioration of gasolines in storage are suggested from the foregoing discussion.   These may be classified as physical (1a and 1b) and bacteriological (2) as follows.   (1a) Lecithin is known to be adsorbed on the gasoline side of the interface, where it may serve as an inert layer which retards the diffusion of oxygen and/or oxidation products from the interface to the main body of the gasoline.   (1b) It is also possible that the large molecules of lecithin may aid in orienting or stabilizing the orientation of the phenolic groups of the inhibitors at the interface. (2) Most of the micro-organisms which are present in gasoline storage tank waters are soil bacteria.   Lecithin is easily hydrolysed by soil bacteria to produce glycerol, fatty acids, phosphoric acid, and choline.[21]   It is suggested that lecithin may have a beneficial effect on gasolines which would otherwise be subject to bacterial action by being preferentially attacked, thereby sparing the hydrocarbons from oxidation.   It is reported

that lecithin is also effective as an inhibitor when gasolines are stored dry. It is general refinery practice to divert finished motor fuels to tank farm storage over water before they are measured into drums for shipment. During this storage over water gasoline is subject to bacterial action. The gasoline may also become contaminated by extracting detrimental oxidative enzymes into the gasoline phase. These enzymes would then be carried into the dry storage with the gasoline. Since all bacterial action may be considered as being enzymatic and many of the enzymes produced by bacteria are gasoline-soluble, it is possible that dissolved lecithin could exert a similar beneficial effect on dissolved oxidative enzymes in contaminated gasolines stored dry.

METAL DEACTIVATORS.

The use of disalicylal ethylene for the deactivation of copper, iron, cobalt, and vanadium has been described by Downing, Clarkson, and Peterson.[22]   Traces of these metals, particularly copper, in gasolines have a very severe effect on its storage stability.   Any of the metals which these authors have named may constitute the metallic atom in the porphyrin enzymes.   The porphyrin enzymes are very active biological oxidation and reduction catalysts which are formed by bacterial as well as other forms of life.   The porphyrins are very widely distributed in nature,[23] and their solution or dispersion in gasoline as a result of bacterial action seems quite likely.   It appears possible that these metals may actually be present in the gasoline in the form of their porphyrin compounds.   Disalicylal ethylene might then deactivate these several metals by some reaction with the porphyrin molecule which would reduce its activity as an oxidation-reduction enzyme.   This hypothesis presents an interesting topic for future research.

SUMMARY.

A new theory is presented to account for the delay in the deterioration of gasoline motor and aviation fuels which is produced by the addition of inhibitors.   The bactericidal properties of the commercial inhibitors are noted.   Data are presented to show that these inhibitors are strongly adsorbed at the gasoline–water interface where they are able to exert their greatest bactericidal activity.   The microbiological aspects of inhibitor intensifiers and metal deactivators are also discussed.   This biological concept of gasoline inhibitors is intended to supplement the extensive chemical research which has been conducted on the deterioration of gasoline motor fuels in storage.

ACKNOWLEDGEMENT.

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THE ANALYSIS OF LIQUEFIABLE HYDROCARBONS BY DISTILLATION.

By the Liquefied Gases Panel of Sub-Committee No. 3.—Liquefied Petroleum Gases, Gasoline, Kerosine, and Light Distillates.

A Panel of Sub-Committee No. 3 of the Standardization Committee has been concerned for some time with methods for the examination of Petroleum Gases. This Panel, which is composed as follows :

> W. H. Thomas (*Chairman*) (Anglo-Iranian Oil Co., Ltd.).
> J. W. Armstrong (Imperial Chemical Industries, Ltd.).
> N. Aston (Esso European Laboratories).
> J. H. D. Hooper (Anglo-Iranian Oil Co., Ltd.).
> N. E. Jones (Trimpell, Ltd.).

has devoted much attention to formulating a procedure which would be generally acceptable for the analysis by distillation of liquefiable hydrocarbon gases. The apparatus used for this purpose is diverse in form and complexity, and various types are used, according to the nature of the product being examined, the precision of the results desired, and the resources of the laboratory concerned.

It was concluded, therefore, that it was neither practicable nor desirable at the present time to attempt to standardize any particular form of apparatus or to lay down, in the detail normally associated with Standard Methods, the procedure for carrying out the determination of these light hydrocarbons.

It may in the future be possible to do this, but in the meantime the Panel felt that it was desirable to formulate a general procedure which should be applicable to any reliable method for distillation analysis and to agree on the best available data for the boiling points and densities of the hydrocarbons for use in calculation. This view was agreed by Sub-Committee No. 3 and by the Standardization Committee.

The following method is published for information, and it is suggested that analysts who are interested in this aspect of the work should send any comments or criticisms to the Secretary of the Institute for consideration by the Sub-Committee and Panel concerned.

It should be noted that many points of distillation technique described in this paper have been taken from a paper by Savelli, Seyfried, and Filbert entitled " Methods of Light Hydrocarbon Analysis " (*Industr. Engng Chem. Anal.*, 1941, 13, 868), and acknowledgment must therefore be made to these authors.

E. B. Evans.

Chairman, Standardization Sub-Committee No. 3.

PRINCIPLE

This method involves the distillation of gaseous and liquid hydrocarbon mixtures into fractions which consist essentially of hydrocarbons containing the same number of carbon atoms. The olefine content of each fraction is determined by means of an Orsat type of constant-pressure gas analysis apparatus, and the data thus obtained, supplemented by the distillation curve, afford an accurate analysis.

APPARATUS.

Several different models of low-temperature fractional distillation apparatus are available, some being fitted with automatic devices for controlling column pressure, reflux cooling, distillation rate, etc., and others being entirely manual in operation. The apparatus consists essentially of a distilling bulb of from 15 ml. to 100 ml. capacity, and a vacuum jacket enclosing a column containing a wire packing. The column head is fitted with means for cooling, to provide reflux to the column, and the outlet therefrom is manifolded to manometers, a distillation rate control valve or cock, distillate receivers, vacuum pump, and sample burettes or Töpler pump for sample removal. The distillate receivers may be either vacuum bottles, generally of 1- and 3-gallon capacity, or large graduated burettes in which the distillate is collected by displacement of a suitable confining liquid, such as mercury, brine, or saturated zinc sulphate solution. A thermocouple is provided for recording the column head temperature.

PROCEDURE.

The individual instructions issued with each apparatus should be followed as closely as possible. The following gives a general outline of the procedure and indicates the factors which are necessary for good fractionation.

The apparatus is evacuated and tested for leaks. If it is gas-tight, the column head and distilling bulb are cooled strongly by means of liquid nitrogen. If this is not available, liquid air may be used instead, but in view of the dangers attending the employment of this material in close proximity to liquid petroleum products, the following precautions should be rigidly observed :

(1) The distilling bulb must never be allowed to come into direct contact with liquid air; it should be enclosed in a protecting metal or pyrex glass sleeve.

(2) When purging the sample entry line, care should be taken that the vented gas is not condensed by the liquid air used for cooling the distilling bulb.

(3) Some non-inflammable material such as glass wool should be used for lagging at the mouth of the Dewar vessel enclosing the distilling bulb. On no account must cotton wool be employed for this purpose.

As commercial liquid nitrogen may also contain an appreciable percentage of oxygen, it is recommended that the above precautions should also be observed with this material.

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Samples may be introduced into the bulb in the liquid form (after the removal of H_2S), but are normally charged to the apparatus in the gaseous state, and are condensed in the distilling bulb after passing through caustic alkali solution and calcium chloride for the removal of acidic constituents and moisture. If uncondensable gases are present, the column pressure will rise; it should be maintained substantially at atmospheric pressure by allowing the gas to pass into one of the receivers while the remainder of the sample is being liquefied. When at least 10 ml. of the liquefied sample have been admitted into the distillation bulb, the sample inlet is closed, and the receiver manifold isolated from the column. The refrigerant is now removed from the Dewar vessel enclosing the distilling bulb and the empty vessel replaced round the bulb.

The distillation is now commenced by switching on the current to the electrical windings attached to the bulb. The column pressure rises as the charge becomes warm, and is brought to atmospheric pressure by releasing uncondensable gases to the receiver. When the column has been brought to equilibrium under *total reflux* by warming the distilling bulb and chilling the column head, until the whole length is wet with reflux, the receiver pressure is recorded for the uncondensable gases. The gas is now distilled at about 20 ml. per minute and allowed to pass over into the distillate receiver. During the distillation, temperature and pressure shall be recorded at frequent intervals, to provide data for the distillation curve.

In order to achieve consistently accurate results from the column, the following standardized procedure, with modifications as noted according to the nature of the sample, must be rigidly followed :

(1) When charging the sample, the following points are of importance :

(*a*) The sample entry line should be as short as is conveniently possible.

(*b*) The contents of the distilling bulb must not be allowed to blow back down the sample entry line.

(*c*) When samples of liquefied gas are withdrawn from pressure-type containers, the sample should be taken from the bottom of the container—*i.e.*, from below the surface of the liquid.

(*d*) Liquefied gases containing any appreciable quantity of C_5 or C_6 components should be charged directly to the apparatus through as short a line as possible, as passage through the normal scrubbing train may result in the partial condensation of these components.

(2) After charging the sample, the temperature in the bulb and head of the column are so balanced that the column is operated under total reflux at slightly reduced pressure (about 100 mm. less than atmospheric) for a period of time depending on the nature of the sample. This is particularly useful for butane separations. A period of 30 minutes is usually sufficient. The pressure in the column is then slowly increased to atmospheric, and the distillation is begun with the temperature in the head of the column at the boiling point of the

lightest component in the sample. If the sample contains large quantities of methane, the distillation may be started without bringing the column under total reflux.

(3) During the distillation, every effort should be made to avoid large fluctuations in the column pressure, and it is therefore recommended that the apparatus be fitted with some system of automatic pressure control. Reflux ratio should be maintained at 15 : 1, and apparatus for measuring this ratio must be provided unless special provision has already been made by the manufacturer of the apparatus.

(4) During the distillation, the temperature in the condenser section of the column, as recorded by the millivoltmeter or potentiometer, is taken as an indication of the purity of the overhead product, and on plateaux is maintained as near as possible to the true boiling point of the component being withdrawn. If on a plateau the temperature should rise above the boiling point of the component being withdrawn, the take-off should be discontinued immediately and the column operated under total reflux until the temperature returns to its former value. The distillation should then be resumed at a slower rate. If the temperature should again rise, this procedure should be repeated until a take-off rate, which will maintain the plateau temperature at a constant value, has been established or until a break is certain.

The boiling points (at 760 mm. Hg) of the lower hydrocarbons may be taken as :—

Methane	.	.	.	.	.	$-161 \cdot 4$
Ethylene	.	.	.	.	.	$-103 \cdot 9$
Ethane	.	.	.	.	.	$- 88 \cdot 9$
Propylene	.	.	.	.	.	$- 47 \cdot 7$
Propane	.	.	.	.	.	$- 42 \cdot 2$
isoButane	.	.	.	.	.	$- 11 \cdot 8$
isoButene	.	.	.	.	.	$- 6 \cdot 8$
Butene —1	.	.	.	.	.	$- 6 \cdot 3$
Butene —2 (mean value)	.	.	.	$+ 1 \cdot 0$
Butadiene 1–3	.	.	.	.	.	$- 4 \cdot 5$
n-Butane	.	.	.	.	.	$- 0 \cdot 5$
isoPentane	.	.	.	.	.	$+ 27 \cdot 95$
n-Pentane	.	.	.	.	.	$+ 35 \cdot 95$

(5) In general, the following take-off rates, at atmospheric pressure, will be found to be satisfactory.

Breaks	.	.	.	— 2– 5 ml. gas/minute.
Plateaux	.	.	.	—10–20 ml. gas/minute.

but it will be appreciated that at pressures lower than atmospheric, reduced rates will be required. Where, however, plateaux are known to be long, the maximum figure of 20 ml./minute may be considerably exceeded, but immediately the column-head temperature shows any

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tendency to rise, the column must be shut in and the rate reduced, as described above.

(6) When a break between components is imminent (as indicated either by a decrease of pressure in the column or by a " thinning out " of the reflux on the column packing, or both), the column should be operated under total reflux for several minutes while the boiling rate in the bulb is reduced.   By reducing the boiling rate, the liquid reflux on the column packing is further " thinned out," thus materially reducing the column hold-up (while maintaining a high reflux ratio) and increasing the sharpness of the break.   After these conditions have been established, the take-off is again begun at a very slow rate, and continued until the break is completed.   (*Note.*—If it is desired to isolate the various fractions, the distillate receiver should be changed when the cut point temperature is attained.)   For columns fitted with automatic take-off controls, the above procedure may, of course, be considerably modified, and, in particular, when distilling samples containing large quantities of methane, ethane, or propane. For such samples, the distillation conditions may be so controlled on plateaux (by controlling the heat input) that the boiling rate is automatically reduced when approaching a break.   Under these conditions, the necessity for operating the column under total reflux will be obviated.

(7) The fractions may be collected in different burettes, and their volumes measured at atmospheric pressure by suitable manipulation of mercury, brine, or zinc sulphate solution reservoirs, or they may be collected in large evacuated bottles maintained at constant temperature.   The distillation is stopped temporarily at each cut point while the receiver is changed or re-evacuated.   Frequent readings of temperature and pressure should be taken throughout the breaks, so that an accurate distillation curve can be plotted.

(8) The pressure in the receiving system should be kept, by repeated evacuation, if necessary, so low that the partial pressure of any constituent is far below that pressure at which it will condense at the temperature of the receiver.   The maximum pressures recommended are :—

$$C_1, C_2, \text{ and } C_3 \quad . \qquad . \quad -\text{Atmospheric pressure.}$$
$$C_4 \quad . \qquad . \qquad . \qquad . \quad -300 \text{ mm. Hg. (absolute).}$$
$$C_5 \quad . \qquad . \qquad . \qquad . \quad -100 \text{ mm. Hg. (absolute).}$$

After each reduction in pressure, the column is operated under total reflux for at least 15 minutes, to bring it to equilibrium.

(9) At the conclusion of the distillation the bulb is filled with mercury to reduce dead-space errors, and any residual reflux on the packing and gas in the column is drawn over into a fresh evacuated receiver.

(10) When a sample is distilled under the above conditions, the appearance of the finished distillation curve is taken as the best indication of the fractionation, and hence analytical accuracy, obtained during the analysis.   In appearance, this curve should have the following characteristics :

(*a*) The plateaux should be horizontal, with few fluctuations (such as are caused by excessive pressure variations, flooding in the column and other undesirable operating conditions), and should show no rise in temperature, even when approaching a break.

(*b*) Breaks between components should be sharp, exhibiting little " sloughing off " at the plateaux, except in the case of separations between isomers or between paraffins and olefins containing the same number of carbon atoms.

Samples of the various fractions obtained will normally require to be analysed for individual components such as hydrogen, olefins, etc., in the appropriate auxiliary apparatus.

CALCULATION OF RESULTS.

Provided that the distillation is carried out under the conditions laid down in paragraph (8) above, the gases are assumed to obey the perfect gas laws, and the increases in pressure in the receiver for each fraction are assumed to be proportional to the volumes of those constituents in the total gas. The amount of sample taken is given by the total pressure rise in the evacuated receivers (differences in size between the various receivers being duly corrected for), and the volume percentage of each gas can thus be obtained.

If it is desired to express the results as weight percentages, it is necessary to convert the pressure rise equivalent to each constituent to the appropriate weight by the formula :—

$$\text{Weight in gm. of constituent } A = \frac{Pf \times Ca \times V \times 273 \times MWa}{760 \times K \times 22,410}$$

where Pf = rise in pressure in mm. representing fraction containing A.

Ca = volume percentage of A in fraction.

hence $Pf \times Ca$ = rise in pressure in mm. due to A.

V = total volume in ml. of receiving bottle and lines to still-head tap.

hence $\dfrac{Pf \times Ca \times V}{760}$ = volume in ml. of A at 760 mm. pressure.

K = absolute temperature (Kelvin scale) of receiving bottle.

hence $\dfrac{Pf \times Ca \times V \times 273}{760 \times K}$ = volume in ml. of A at 760 mm. pressure and °C.

MWa = molecular weight of A.

$22,410$ = gm. molecular volume in ml.

To obtain the results as liquid volume percentages at 60° F., the following proposed specific gravities at 60° F. may be used :—

Methane	0·3
Ethylene	0·390
Ethane	0·374
Propylene	0·5215
Propane	0·5073
*iso*Butene	0·603
Butene —1	0·600
Butene —2	0·615 (mean)
i-Butane	0·563
n-Butane	0·584
Pentenes	0·658 (mean)
i-Pentane	0·625
n-Pentane	0·631
i-Hexane	0·658
n-Hexane	0·664

REVISED CLASSIFICATION OF ABSTRACTS

(Prepared by Mr. C. L. Gilbert on behalf of the Abstracts Sub-Committee)

THE Abstracts Sub-Committee has decided to make some changes in the headings under which the abstracts are classified, and these are being brought into operation in the current number of the *Journal*. Difficulties arose in the previous system for two reasons : (1) separate headings were provided for products and the treatment of products, and it was thus not clear whether, for example, the refining of motor fuels should be placed under Refining or under Motor Fuels; (2) the field to be covered by some of the product headings was not clear, *e.g.* the distinction between Synthetic and Special Products.

An attempt has therefore been made to define more precisely the field to be covered by each heading. Additional headings have been provided where necessary, and, while some of the present headings have been dropped, most of them have been retained for convenience.

As will be seen from the list at the foot, the subject matter has been divided into six main categories, these roughly following the stages in the treatment of petroleum and allied products. Each of these is then divided further as required. A few notes on these headings may assist in showing where data required may be located in the abstracts.

Oilfield Exploration and Exploitation.

This main heading covers the original headings, Geology and Development, Geophysics, Drilling, Production and Aerial Survey. In the new system Development has been separated from Geology, as it logically follows Production, whereas Geology comes first. Aerial Survey is now included in Geology.

Transport and Storage.

No change.

Refinery Operations.

In this main section are placed data on the refining of any product, petroleum or otherwise, *i.e.* if it is a question of refining, it is placed here rather than under the product name. A number of changes and additions to the sub-headings have been made. Thus the original Refining and Refinery Operations is now restricted to general descriptions of refineries, and of auxiliary refinery equipment. New headings have been made for Chemical and Physical Refining; Distillation; Solvent Extraction and Dewaxing; Adsorption and Absorption; Isomerization; and Special Processes, while Polymerization and Alkylation have been separated. The heading Metering is now expanded to include Control, while Fire Prevention is dropped as this is logically included in Safety Precautions.

Products.

This section covers only the properties and uses of products (including patents relating thereto), their manufacture being placed in the previous

section.   The headings Chemistry and Physics and Analysis and Testing apply to all products, whether petroleum or otherwise.

Under Crude Oil will be placed data only on its properties.   Under Gas will be placed data on all gases other than those used as motor fuels.

The heading Motor Fuels has been superseded by the heading Engine Fuels, and this now includes Diesel Fuels.   Information previously placed under the heading of Detonation and Engines will go either under the Engine Fuels heading or under a separate heading—Engines.

The next heading then becomes Gas Oil and Fuel Oil.   It will be noted that oils for high-speed diesel engines are not included here, but under Engine Fuels.

The old heading Lubricants and Lubrication has been shortened to Lubricants, the subject of Lubrication being implied as a property of a Lubricant.

The heading Asphalt and Bitumen has been expanded to include Tar under the new arrangements, whereby allied products of all sources are included under the new product headings.   This heading will also include information on emulsions, products containing bitumen or normally associated with them, such as soils, aggregates, etc.

The heading Special Products has been divided into Special Hydrocarbon Products and Derived Chemical Products, the former including Hydrocarbon materials such as kerosines, white spirits, wax extracts, spray oils, etc., and also including ingredients normally used with these products (*e.g.* Pyrethrum used in fly sprays).   The heading Derived Chemical Products includes non-Hydrocarbon Products obtained from Petroleum and allied products.

A further category of Miscellaneous Products is provided for manufactured products which cannot be classified under the above headings, such as Paints, Synthetic Rubbers, Plastics, Synthetic Fibres.

Engines and Automotive Equipment.

This heading covers the appropriate part of the original heading Detonation and Engines, but it is hoped to expand it to include any new Automotive Equipment of interest, *e.g.* cars, aeroplanes, etc.   Road tests on new equipment will also be included here.

Miscellaneous.

This main heading is for information on Petroleum from the point of view of history, economics, statistics, legislation, specifications, marketing, etc.

CLASSIFICATION OF ABSTRACTS

Main Heading.	*Sub Heading.*
EXPLORATION AND EXPLOITATION	Geology.
	Geophysics and Geochemical Prospecting.
	Drilling.
	Production.
	Oilfield Development.
TRANSPORT AND STORAGE	

REFINERY OPERATIONS

- Refineries and Auxiliary Refinery Plant.
- Distillation.
- Absorption and Adsorption.
- Solvent Refining and Dewaxing.
- Cracking.
- Hydrogenation.
- Polymerization.
- Alkylation.
- Isomerization.
- Chemical and Physical Refining.
- Special Processes.
- Metering and Control.
- Safety Precautions.

PRODUCTS

- Chemistry and Physics.
- Analysis and Testing.
- Crude Oil.
- Gas.
- Engine Fuels.
- Gas Oil and Fuel Oil.
- Lubricants.
- Bitumen, Asphalt, and Tar.
- Special Hydrocarbon Products.
- Derived Chemical Products.
- Coal, Shale, and Peat.
- Miscellaneous Products.

ENGINES AND AUTOMOTIVE EQUIPMENT

MISCELLANEOUS.

CORRIGENDUM.

" Sintered Glassware." By I. C. P. SMITH, *J. Inst. Petrol.*, December 1944, 30(252), 387.

The last sentence of the paragraph entitled " An Emulsifying Machine " should read as follows : " Application has been made for a patent to cover this particular use of sintered glassware."

OBITUARY.

SIR JOHN JACOB FOX, C.B., O.B.E., D.Sc., F.R.S.

WE regret to announce the death of one of our senior honorary members, Sir John Jacob Fox, C.B., O.B.E., D.Sc., F.R.S., the Government Chemist.

He was born in 1874 and entered the Government Laboratory in Clements Inn in 1904. He succeeded a former honorary member, Sir Robert Robertson, as Government Chemist in 1936. During the war he served in many capacities in Departments of State and contributed widely from his long and unique experience in chemical science and technology.

The writer of this note would rather remember Fox as a very genial and kindly soul who, indeed, regarded most of his contemporaries and juniors as his own friends. The writer's memory goes back forty years to the time when he and Fox worked side by side in the research laboratory of another genial and friendly soul, Emeritius Professor Hewitt, of Queen Mary College, when two other members of Council—Col. Auld and Dr. Thole—were fellow students with him.

Only a few months ago many of Fox's co-workers assembled to pay honour to him on the conferment on him of Knighthood and the Fellowship of the Royal Society, and it is sad to think that so soon afterwards he passed over.   A. E. D.