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GUM PROBLEM IN MOTORFUELS: RATE OF DISTILLATION REFLECTED IN AMOUNT PRESENT. PREPONDERANCE OF

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Gum Problem in Motor Fuels

Rate of Distillation Reflected in Amount Present. Preponderance of Constituents Found in Certain Fractions

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FACTORS IN GUM FORMATION

There are two or more kinds of gum in gasolines and apparently one kind can form without affecting the unsaturation of the gasoline (as determined with **sulphuric acid**).

The rate of distillation or fractionation has an effect on the amount of gums formed in the gasoline and it is believed that polymerization takes place during a slow distillation so that the polymerized products may be separated by virtue of their boiling points.

A preponderance of gum-forming constituents occurs in certain fractions of a gasoline and it is possible to segregate these fractions. It is thus possible to separate the gum-forming fractions of a gasoline and treat each fraction as needed.

As the fractions containing the gum-forming constituents do not have the same distillation range for **all gasolines, no general rule can** be followed in fractionating gasolines, but it is necessary for each refiner to make a study of the distillates he is using and fractionate accordingly.

Gums and gum-forming compounds, if they occur in motor fuel, give rise to many refining and utilization problems. Deposits in storage tanks, piping, carburetors, etc., may occur; motor valve stems, especially if the valves leak slightly, may become coated with a sticky gum which impedes their action, and gasoline pump bowls may become discolored.

Refiners have had trouble with gums and gum-forming compounds for many years, especially since "cracked" gasoline has been placed on the market. Vapor-phase cracked products seem to have a greater tendency to form gums than those cracked by the liquid-phase cracking process. The percentage of unsaturated hydrocarbons is usually greater in the products from vapor-phase cracking at higher temperatures than in gasolines produced by liquid-phase cracking processes.

Considerable work has been done by different investigators on gum and gum-forming compounds, but up to the present time it has not been definitely proved just what compounds cause the formation of gums, although it is generally assumed by refiners that the diolefines are the parent substances from which most of the gums in gasoline are formed. It seems probable that there are several different kinds of "gum," each of which is formed in a different manner or from different compounds.

Types of Gum

One type of gum, that which develops when gasoline is evaporated or stored in the presence of air has been studied by Smith and Cooke[1] who came to the con-aldehydes formed by the oxidation of olefines or diolefines. Apparently this is not so with all products as the authors of this paper have tested several samples of gasolines that contained gums and other samples that formed gums, and were unable to detect aldehydes. Brooks[2] states that the first step in the formation of gum in cracked gasolines is the formation of organic peroxides and that the gum is merely the end product of polymerized peroxides.

In regard to the gums formed by oxidation Smith and Cooke[3] state:

"The amount of unsaturated hydrocarbons present in a sample of gasoline is usually estimated by determining the solubility of the gasoline in concentrated sulphuric acid. In order to ascertain if the amount of gum that could be made from a sample of gasoline had any relation to the 'unsaturation,' as so determined, a sample was heated for 100 hours in the presence of water with a current of air passing through it. At the end of this time the sample was decanted from the separated gum and then distilled in a current of 'open' steam so that any gum that had formed in the gasoline itself could be recovered. The distillate from the steam distillation was again oxidized in the presence of water for 100 hours, and this process was repeated until more than 7 per cent of gum had been obtained. The 'unsaturation' of the original gasoline was 18 per cent; the 'unsaturation' of the gasoline from which 7 per cent of gum had been made was 17 per cent. This result indicates that there can be no quantitative relation between the so-called 'unsaturation,' as measured by solubility in sulphuric acid, and the amount of gum that can be made. To check this point, two samples of gasoline were prepared. One sample was a distillate boiling between 140° C. (284° F.) and 170° C. (338° F.). This product was thoroughly treated with acid and alkali, and after being thoroughly washed it was steam distilled over caustic potash. It was an absolutely water-white product with an entirely sweet odor. The 'unsaturation' was less than 1 per cent. The second sample was prepared by stilling cracked gasoline over caustic potash. This sample had an 'unsaturation' of 18 per cent. Each of these samples was oxidized by heating under a reflux condenser on a steam bath with a gentle current of air for 300 hours. The cracked gasoline which originally had 18 per cent of 'unsaturation' developed [illegible] per cent of gum, and the 'unsaturation' of the residual gasoline was still 18 per cent. The saturated gasoline developed 0.97 per cent of gum, and in the process developed an 'unsaturation' of 8 per cent.

"These figures confirm those reported above, that there is no direct connection between 'unsaturation' as determined by solubility in sulphuric acid, and the percentage of gum that can be formed from gasoline. It should be noted, however, that the authors have not attempted to measure the amount or kind of "unsaturated' hydrocarbons present in gasoline. The sulphuric acid test is empirical and may indicate the presence of many compounds other than 'unsaturated' hydrocarbons."

The tests just quoted were made under conditions that would not occur in the commercial refining, storage and use of motor fuel. They indicate, however, that while there is no quantitative relation between "unsaturation" and gum formation, nevertheless, the "saturated" material was much more resistant to gum formation.

Other information, however, obtained in the laboratory and from the literature seems to show that certain types of gums are caused or formed from unsaturated hydrocarbons. Treatment of cracked gasolines with acid usually removes the gum-forming constituents; vapor-phase treatment with fuller's earth polymerizes these constituents to higher boiling compounds which are removed from the gaso-

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[1] Smith, N. A. C., and Cooke, M. B., Gum-Forming Constituents in Gasoline. Bureau of Mines Reports of Investigations, Serial No. 2,394, September, 1922.

[2] Brooks, B. T. The Chemistry of Gasolines. Ind. and Eng. Chem., Volume 18, No. 11; November, 1926, Page 1,198.

[3] Smith, N. A. C., and Cooke, M. B. Work cited.

line vapors by virtue of their high boiling points.

The gum determination methods now in use indicate the amount of gum in the gasoline at the time the test is made, together with additional gum that may develop during the test itself. There is a great difference between the gum content as determined by laboratory tests and the amount of gum formed in gasoline on standing.

Methods of Gum Determination

The two methods commonly used at present are the copper-dish and the steam-oven methods, both of which are in general use by refiners in determining the gum content of gasolines. The copper-dish method is perhaps the most widely used. Dean[4] states that the copper-dish method was devised by F. C. Robinson and his associates of the Atlantic Refining Co. as one of the tests used for aviation gasoline. The copper-dish method as ordinarily run usually shows more "gum" than the actual gum content of the product. This is especially true in products containing sulphur or sulphur compounds, because sulphur and sulphur compounds unite readily with copper and form copper sulphides. As the gum content of the product is determined by the increase in weight of the dish, it is evident that a large part of the increase in weight may be due to copper sulphide. Furthermore, there is a chance for oxidation of the heavier fractions of the gasoline during evaporation, which results in a marked increase in the weight of gum in the dish.

In the steam-oven method devised by Cooke[5] for making gum determinations a sample of the gasoline is evaporated in a glass dish in an atmosphere of steam.

The oxidation method developed by Voorhees and Eisinger[6] determines the gum-forming properties of a gasoline by heating it in contact with oxygen for a certain period. This method will give an indication of the amount of gum that may form in gasoline on standing in storage. Of the different methods so far devised for determining gums in gasoline the glass-dish method as devised by Cooke[7] or with slight modifications seems to be the most reliable. This method gives the amount of preformed gum in the gasoline at the time of test plus that which may form in the gasoline while the test is made. The oxidation method of Voorhees and Eisinger[8] is one of the best methods so far devised to determine the potential gum content of a gasoline.

The amount of gum that will form in a gasoline in storage will depend on the compounds in the gasoline and the length of time it stands in storage. Sunlight accelerates the formation of gums and gasoline exposed to sunlight will develop more gum than if it is stored in darkness. Most investigators agree that it is the preformed gum in a gasoline that causes the most trouble when gumming gasolines are used as motor fuels. This being the case, gasolines that are held in storage for a considerable period of time before use should be so refined that the possibility of forming excessive amounts of gum be eliminated.

Use of Inhibitors

Considerable interest has been shown during the last few months in the use of chemical inhibitors for the prevention of the formation of gums in gasoline in storage.

Apparently considerable work has been done by different investigators along this line but not much has been published. The information available, however, indicates that such antioxidants as α-naphthylamine, hydroquinone, and phenols seem to have the best possibilities along this line.

The rubber industry has done a lot of work on the use of antioxidants and it is possible that considerable information which may be obtained from this source will be of *value to the petroleum* industry.

Any antioxidant to be of economic value to the petroleum industry must be one that is cheap and powerful so that it is necessary to add only a very small percentage to the gasoline to accomplish the desired result. Tests made by the authors indicate that in general a slow rate of distillation has a most beneficial effect on color stability and on the elimination of gums from gasoline. Polymerization may account for this. In a slow distillation where the vapors are condensed and revaporized often, the color and gum-forming constituents in the gasoline may be changed to higher boiling point products.

Application of this method can be made in the distillation of gasolines in the refinery but the question as to what extent one can reduce throughput in order to make a product requiring less chemical treatment is an economic one that each refiner with his own particular equipment and set-up must work out.

Distribution of Gums

If gum determinations are made on similar gasolines by either the copper-dish or steam-oven method, it is noticeable that the higher the boiling point of the product the higher the percentage of gum, especially in cracked gasoline. However, the amount of gum that settles out when samples of gasoline are allowed to stand in storage does not depend on the boiling range of the product. If a sample of gasoline is fractionated in 10 per cent cuts and gum determinations are made on each cut, the heavier fractions will show the greatest percentage of gum. On the other hand, if these same fractions are allowed to stand exposed to sunlight, some of the lighter fractions may show the greatest percentages of gum and no gum may be formed or settled out of some of the heavier fractions. In addition, the fractions in which the gums form and settle out on standing do not have the same place in the distillation range for all gasolines.

Treated gasolines often show a greater percentage of gums than untreated gasolines; especially if the gasoline has been treated according to the doctor method of sweetening and an excess of sulphur has been added at the time of treating.

Cracked gasolines that have been treated with hypochlorite often show a greater percentage of gum than untreated gasoline unless the strength of the hypochlorite has been carefully controlled. Gasolines may be treated in the liquid phase with *absorptive materials such* as fuller's earth and silica-gel, and the color will usually be improved, but this treatment apparently often starts a polymerizing reaction, and after standing the percentage of gum may increase. In gasolines made from acid-treated pressure distillates gums quite often settle out and the color becomes unstable. This may be attributed to esters formed as a result of the acid treatment and dissolved in the gasoline. It has been observed by the authors that the formation of gums and color instability can be appreciably reduced if, when rerunning acid-treated pressure distillate, the gasoline vapors as they come from the still are washed with water. Probably the esters are dissolved by the water and thus removed from the gasoline. The use of water produces results in this respect as beneficial as a steam distillation. The use of a caustic wash also reduces the formation of gums.

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[4] Dean, E. W., Motor Gasoline Properties. Laboratory Methods of Testing and Practical Specifications. Bureau of Mines Technical Paper 214, Page 25.

[5] Cooke, M. B. A Convenient Method for Determining Gum-Forming Material in Gasoline. Bureau of Mines Reports of Investigations, Serial No. 2,686, May, 1925.

[6] Voorhees, V., and Eisinger, J. O. The Importance and Significance of Gum in Gasoline. American Petroleum Institute Bulletin 1,929-10, No. 2, 169.

[7] Cooke, M. B. Cited.

[8] Voorhees, V., and Eisinger, J. O. Cited.

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