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METHOD FOR INHIBITING GUM FORMATION IN LOW BOILING HYDROCARBON OILS AND PRODUCTS OBTAINED THEREBY

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2 Claims. (Cl. 44—9)

The present invention relates to a method of inhibiting or retarding gum formation in low boiling hydrocarbon liquids. The invention in its preferred form includes indicating colorimetrically that protection against gum formation is being afforded. It also includes products prepared by the method.

It has long been well known in the petroleum industry that low boiling hydrocarbon liquids such as gasoline and naphtha, especially cracked gasoline and naphtha, often contain gum or gum forming constituents in harmful quantity. In the following description, the liquid to be treated will be referred to as low boiling hydrocarbon liquid or naphtha. It is to be understood, however, that the principles of the invention may be applied to other liquids of analogous character.

Naphthas containing large quantities of gum, or constituents tending to form gum during storage, are objectionable for many purposes, such as for motor fuels, light solvents, etc. Recently a careful study of gum formation has been made by petroleum chemists, and several organic compounds nave been found which, when added in small quantities to low boiling hydrocarbon liquid, will retard or inhibit gum formation for periods of time varying with the nature of the compound, the liquid, and other conditions.

According to the present invention, improved inhibiting effects are obtained by the use of certain organic compounds usually classified as dyes. These will be fully described hereinafter, both by their chemical constitution and by their inhibiting effect. The tests for the latter will first be given.

The usual test for such gum forming constituents is known as the copper dish method and is described on page 96 of the United States Bureau of Mines Technical Paper No. 323D, revised October 21, 1927. The result of this test is expressed in milligrams of gum left in the dish on evaporation of 100 cc. of naphtha.

Another testing method consists of adding oxygen under pressure to the sample of the low boiling hydrocarbon liquid to be tested in a closed vessel, and then keeping the liquid at elevated temperature of say 100° C. under a pressure of oxygen of say 100 lbs. per square inch. For a certain time the pressure remains practically constant, then it begins to drop suddenly. This drop is observed on a pressure gage. The period of time during which no pressure drop is observed is called the induction period. The longer this induction period, the better is the particular liquid tested, and the less likely it is to form gum during storage.

An approximate quantitative relation for the gum inhibiting power of a certain inhibitor may be expressed by the following equation:

$$I.P.=\frac{S-B}{B}\times\frac{1}{C}$$

where I. P.=inhibiting power
S =induction period of solution
B =induction period of blank or solvent
C =concentration of the inhibitor in % by weight.

The test just described is quicker and more reliable, and gives more readily reproducible data, than the copper dish method. The I. P. number of an inhibitor will accordingly be used herein as a measure of its value. It will be understood, however, that the inhibitors of the present invention may be rated according to the copper dish method, or other suitable method, and will show a corresponding value. Moreover, these inhibitors are effective in actual storage tests, that is, when added to naphtha stored in the tanks of refineries or distributors. The oxidation test described herein gives an accelerated indication of the performance to be expected during storage.

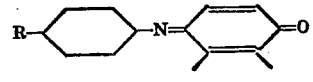
It is a practical experience that the protecting power of the gum inhibitor vanishes after a certain length of time, which may be a very long period in the case of powerful inhibitors. In any case the naphtha on long storage will usually reach such a stage that gum formation begins to set in even though originally a gum inhibitor has been added to the naphtha.

I have discovered that certain dyes are powerful gum inhibitors. The preferred dyes are also characterized by the fact that they are fugitive under conditions of use, that is naphthas colored by them will gradually lose color during storage with exclusion of light, before the inhibiting power of the dye has ceased, i. e., before gum formation sets in. The use of such colored inhibitors has, therefore, the double advantage of inhibiting gum formation for a long period of time and of giving a certain easily observed change in the color of the naphtha when the effect of the gum inhibitor diminishes or vanishes. Not all dyes will show a marked color change before their inhibiting effect is gone. The following types of dyes include good gum inhibitors and have the property of fading, under normal operating conditions, before their inhibiting action in the gasoline ceases:

(1) Indophenols (classes 1 and 2)
(2) Oxazines (bases)
(3) Indamines (bases)
(4) Eurhodines (bases)
(5) Safranines and aposafranines (bases)
(6) Amino azo dyes (bases)

These classes of dyes will be discussed in order.

(1) The indophenols have the general formula:



where R is amino or alkyl amino group in class 1 of these dyes and hydroxyl or alkyl oxy group in class 2. Class 1 of these dyes usually has a blue to violet color and class 2 a red color. Individual members of class 1 of this type may be prepared by condensing a para diamine compound or a para amino dialkyl amine with a phenol having an open para position in a weakly acid (nonmineral acid) solution by means of an oxidizing agent. Class 2 may be prepared by similar condensation of an amino phenolic compound with a phenol. It will be understood that hydroxyl compounds containing condensed nuclei, such as alpha naphthol, are the equivalent of phenol. The following examples may be cited among these types of dyes which exhibited good gum inhibiting properties when added in an amount of 0.0005–0.1% by weight to the naphtha.

Indophenols class I

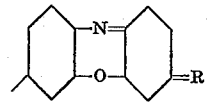
Para amino dimethyl aniline+phenol
Para amino dimethyl aniline+αnaphthol (ordinary indophenol)
Para amino diethyl aniline+phenol
Para amino diethyl aniline+αnaphthol
Para phenylene diamine+αnaphthol
1:4 diamino naphthalene+αnaphthol

Indophenols class II

Para amino phenol+phenol
Para amino phenol+αnaphthol
Para phenetidine+αnaphthol

These dyes are very powerful inhibitors which will fade previous to gum formation. Quantitative tests gave an I. P. number of around 400 for ordinary indophenol and for p-amino phenol+alpha naphthol. Other members of this type, although somewhat less effective than the examples just given, have I. P. numbers amounting to several hundred.

(2) Oxazines are dyes of the following type:



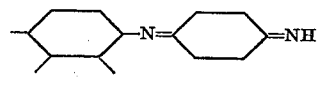
where R is an amino or phenol group and may be obtained by: (1) Condensing and oxidizing a para diamine with βnaphthol and condensing a p-nitrosamine with βnaphthol. (2) Condensing and oxidizing a para diamine with a para substituted phenol. (3) Condensing a nitroso dialkyl m-amido phenol with an aniline or homologue.

These in general must be alkylated to render them oil soluble. The salts are blue, the bases and alkylated bases various shades of red.

Amine	Phenol	Common name
Nitrosodimethyl aniline	Beta naphthol + alkylation.	Meldolas blue + alkylation.
Nitrosodiethyl m-amidophenol.	Alpha naphthylamine.	Nile blue.
Nitrosodimethyl naphthylamine.	Naphthol.	
Nitrosodialkyl m-amino p-cresol.	Ortho or para diamine.	Cresyl blue.

and others

(3) Indamines are compounds of the type:



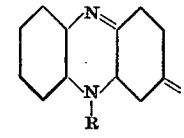
obtained by condensing and oxidizing p-diamines with arylamines or by condensing p-nitrosoarylamines with arylamines. Aryl groups may be mono- or polycyclic, such as benzene or naphthalene and derivatives. Derivatives as in indophenols. Their color is various shades of blue.

Para diamine	Amine	Common name
Para aminodimethylaniline	Dimethylaniline.	Bindeschweiler's green (base).
Para phenylene diamine	Toluylene diamine.	Indamine base for toluylene red.
Para aminodimethylaniline	Toluylene diamine.	Toluylene blue.
Para aminodimethylaniline	Toluylene diamine + alkylation.	

In this type p-aminodimethylaniline+alpha naphthylamine has an I. P. number of 400.

(4) Eurhodines are obtained by the condensing of p-diamines of nitrosoamines with meta diamines and oxidizing the indamine. Alkyl groups may be mono- or polycyclic, such as benzene, naphthalene, and derivatives. Derivatives as in indophenols, except that meta amino groups may not be disubstituted (but may be monosubstituted). Color bases are red in this type. As an example: Nitrosodimethyl aniline+m-toluylene diamine which is commonly known as neutral red has an I. P. number of 209.

(5) Safranines and aposafranines are compounds of the type:



where R is benzene, naphthalene, or aryl group.

Prepared by: (1) Condensation of a para diamine and an aniline (an indamine and an aniline).
(2) Condensation of an amino azo aniline with an aniline.

These must be generally alkylated for use.

Preparation	Common name
Safranines	
Safranine+diethyl sulfate (safranine is obtained by oxidation of ortho and para toluidine to indamine+aniline and oxidation).	Alkylated safranine.
Amino azo alpha naphthalene+alpha naphthylamine.	Magdala red base.
Aposafranines	
Aniline azo alpha naphthalene+aniline+aniline hydrochloride (base).	Azo carmine (unsulfonated base).

In this type of dyes the ethylated safranine has an I. P. value of 2500 and the azo carmine base 1200.

(6) Another type of dyes including good inhibitors are the azo dyes which are prepared in the following manner: A benzenoid amine is treated with nitrous acid in the cold to produce a diazonium compound. This is added to an alkaline, neutral or faintly acid solution of an amine (class 1) or phenol (class 2) containing an open position in a para or ortho position. Class 1 of this type, viz., the amino azo dyes, in-

cludes good inhibitors such as, for example, the ones obtained from:

aniline+alpha naphthylamine,

aniline+alpha naphthylamine, ethylated,

beta naphthylamine+alpha naphthylamine, ethylated,

p-chloraniline+alpha naphthylamine,

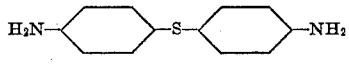
alpha naphthylamine+alpha naphthylamine, ethylated;

the last one being the best.

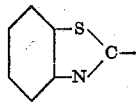
Class 2 consisting of phenolic azo dyes includes dyes, the inhibiting power of which is not so great, and which, furthermore, will not fade previous to gum formation in gasoline.

It will be understood that the specific dyes enumerated are given by way of example and not by way of limitation of the invention since I have actually prepared and found as inhibitors many other compounds of the same types. Their number may be multiplied, not only by means of using homologues or other equivalents in their preparation, but also by introducing various groups, such as for example, amino or hydroxyl groups, further by alkylation, etc. In this connection, however, dyes containing sulfonic acid or thiobenzyl groups must be excluded because these are accelerating groups which may entirely destroy the inhibiting power due to other groups in the dye. In amino compounds the inhibiting power is sometimes increased by alkylation, which also increases the solubility of the dye in oil. The term thiobenzyl is meant to designate an aromatic nucleus with a noncyclic sulphur in the side chain. Typical groups barred under this category are the following types:

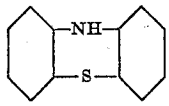
Derivatives of p, p-thio-bisanoline



Thiazoles, such as primulines, containing



Thiazines, such as methylene blue, containing



and similar combinations in which the sulfur is attached to a carbon atom and not in an aromatic ring. For example, thiophene derivatives are not injurious, provided they contain no other injurious groups.

The amounts of the dyes to be added vary in accordance with the gumming tendency of the liquid, the length of time it is required to resist gum formation, and other conditions. In general, the range given above in connection with the inophenol dyes (0.0005–0.1% by weight of the liquid) is suitable for all the classes listed. The amounts must necessarily be determined empirically. The essentials are adequate colorization and inhibition. Any amounts of dyes which accomplish these results are within the intent of this invention.

Many of the dyes are sufficiently oil soluble and may be readily distributed uniformly throughout even large bodies of liquid by simple mixing means. If desirable, the dyes may be dissolved in benzene or other suitable solvent, from which the dye will not be readily precipitated by access of moisture. The solution so prepared may be mixed with the liquid. When sampling indicates that a liquid in storage is losing its dye color, additional dye may be added to prolong the non-gumming period. Variations in dye color and inhibiting effect may be obtained by using mixtures of two or more of the dyes specified.

Various permanent or semi-permanent dyes have heretofore been used to color naphtha. So far as I am aware, none of these dyes has any gum inhibiting effect, certainly none comparable to that obtainable by the use of the inhibitors claimed herein. This effect may be defined as lying in general above the I. P. number 150. In the preferred dyes, the number is in excess of 500, and in the most effective dyes it is in excess of 1000. These effects are characteristic of dyes which are ortho, para, or ortho and para substituted amines.

The present invention includes the indicated dyes, whether or not under the conditions of operation they fade before gum formation begins. Although the invention has been described at length in connection with the preferred type of dyes, namely those which fade before their inhibiting power ceases, it will be understood that the invention comprehends also the use of other inhibiting dyes.

It is known to those skilled in the art that the structural formulas given for the various types of compounds are not the only ones used because such formulas are not universally accepted. There are also variations in the preparation of the compounds. However, the name "compound of indophenol type", for example, gives an adequate understanding to anyone acquainted with this field of chemistry not only of the type of the compound but also how it is made. In the following claims the inhibitors of my invention are accordingly identified.

Coloring matters such as azo dyes have been previously used to retard the decomposition on sunlight of concentrated or dilute solutions of iron carbonyl in gasoline. The present invention relates to the use of specified classes of coloring materials for an entirely different purpose namely for the retardation of gum formation in naphthas which do not contain iron carbonyl in solution.

Having thus described my invention and the method of carrying it out, what I claim is:

1. A composition of matter comprising cracked gasoline of the type which tends to deteriorate on storage as evidenced by gum formation containing as a stabilizer thereof a small quantity of an oxazine.

2. A low boiling hydrocarbon liquid formed by high temperature decomposition of heavy hydrocarbon material and normally tending to form gum on storage, said liquid containing a colored gum inhibitor having the property of fading before its inhibiting power ceases, said gum inhibitor being selected from the class of non-sulfonated organic substances consisting of Meldolas blue, Nile blue and Cresyl blue, said substances bearing no thiobenzyl group.

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