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SWEETENING AND STABILIZING HYDROCARBON OILS

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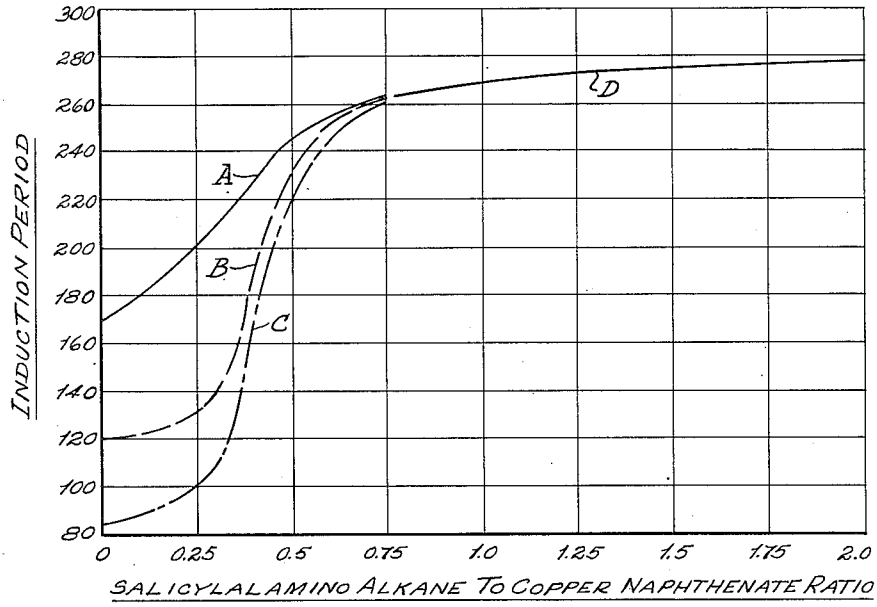


Fig. 1.

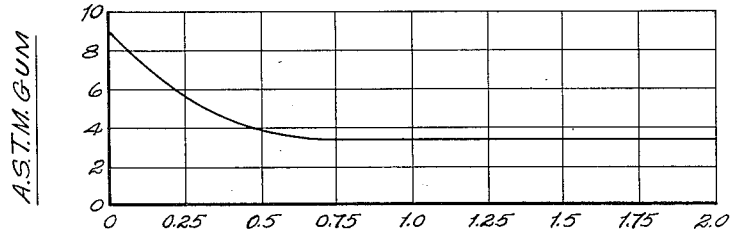


Fig. 2.

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SWEETENING AND STABILIZING HYDROCARBON OILS

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6 Claims. (Cl. 196—30)

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This invention relates to the treatment of hydrocarbon oils, particularly light hydrocarbon oils adapted for motor fuel, and contemplates treating the hydrocarbon oil with an organic metallic salt in combination with certain oxidation inhibitors and metal deactivators to effect sweetening and stabilizing of the oil.

In accordance with the invention light hydrocarbon oil, such as gasoline or naphtha containing mercaptans, is simultaneously contacted with a combination of reagents which includes an organic metallic salt, a phenylene diamine, and a nitrogen-substituted salicylalamino alkane. The organic salts adapted for the practice of the invention include salts of copper, cobalt, lead or zinc, particularly oleates and naphthanates. The phenylene diamine used is preferably a paraphenylene diamine or a dialkyl derivative thereof, such as N,N'dialkyl-para-phenylene diamine. The salicylalamino alkane used is preferably a polysalicylamino polyalkane, such as N,N'disalicylal-1-2 diaminopropane. By treating the hydrocarbon oil with the combination of the three reagents, the organic metallic salt, the paraphenylene diamine or dialkyl derivative thereof, and the N-salicylalamino alkane, a conversion of the mercaptans to produce a sweet product is accomplished while simultaneously a stabilization against oxidation is effected.

The invention is adapted particularly for the treatment of hydrocarbon oil which although sour and yielding a positive reaction in the doctor test contains a relatively small mercaptan content. Thus, the invention is especially adapted to the treatment of such stocks as light naphthas from fluid catalytic cracking operations and low mercaptan straight run naphthas which can be rendered completely sweet and stable against oxidation without other treatment or addition of inhibitors. The process is also adapted as a finishing treatment to sweeten and stabilize stocks which have previously received treatment for the removal of mercaptans such as alkaline treatments. Thus, for example, the well-known solutizer process in which the hydrocarbon is treated with alkali metal hydroxide in the presence of various solutizers does not produce a sweet product and the hereindescribed process is well adapted for treating such product to render it sweet as well as stable against oxidation.

The process possesses a particular advantage in that it does not require the usual agitators or reaction vessels commonly employed in treating processes. Thus, the distillate can be taken directly from the stills or from a preceding treating system and sent to tankage and the process of the invention may be applied by simply introducing the three additives into the transfer line. The materials introduced are soluble in the light hydrocarbon and the mixing in the pipe and in the tank where the distillate is received is adequate to effect the desired dispersion of the treating materials in the oil.

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As showing the effect of the treatment with the materials contemplated in the invention some comparative tests were made in treating a cracked gasoline which had previously received treatment with a metallic alkali hydroxide in a solutizer unit. This gasoline had a mercaptan sulfur content of 0.0015% and showed a positive doctor test both initially and after standing for a period of some 12 hours. It showed a copper dish gum test of 39 mgs./100 cc. and in the ASTM oxidation test had an induction period of 165 minutes. The gasoline was separated into four different portions and each portion was given a different treatment. N,N'disecbutyl - paraphenylene - diamine was added to the first portion in a quantity equivalent to 10 lbs./1000 bbls. of gasoline. The same quantity of the para-phenylenediamine and copper naphthenate in an amount equivalent to 5 lbs./1000 bbls. was added to the second portion. The same quantity of the para-phenylenediamine and N,N' - disalicylal-1-2-diaminopropane equivalent to 5 lbs./1000 bbls. was added to the third portion. All three additives were added to the fourth portion each in the same quantity as used in treating the other portions. (The N,N'-disalicylal-1-2-diamino-propane used was in its commercial form consisting of a solution in xylene, one part xylene to 4 parts active ingredient.) The following table gives the results obtained in the comparative treatments:

Additives	Paraphenylenediamine			
	+Copper Naphthenate		+N-salicylalamino Alkane	+Copper Naphthenate +N-salicylalamino Alkane
Doctor test:				
Initial	Pos.	Pos.	Pos.	Pos.
After 12 hrs.	Pos.	Neg.	Pos.	Neg.
Copper Dish Gum mg./100 cc.	27	36	4	6
ASTM Induction Period	345	35	345	360

It will be seen that the gasoline treated with the paraphenylenediamine only was still not sweet but it had a good induction period. The

treatment with the paraphenylenediamine and copper naphthenate produced a product which was sweet after standing but the induction period was very low. The treatment with the paraphenylenediamine and the N-salicylalamino alkane did not sweeten the gasoline but yielded a product having a good induction period. The treatment with the combination of the three materials yielded a product which was sweet after 12 hours and possessed a good induction period. It might be expected that the metal deactivating effect of the salicylalamino alkane would inhibit the sweetening effect of the copper naphthenate but nevertheless the product was sweet after standing while at the same time the alkyl phenylene diamine did inhibit the oxidizing or gum-forming tendency of the copper naphthenate so that the product had a high induction period.

In the further description of the invention, reference is had to the accompanying drawings wherein:

Figure 1 is a graph showing the effect on the induction period of varying proportions of salicylalamino alkane to copper naphthenate.

Figure 2 is a graph showing the effect on gum formation in varying the ratio of salicylalamino alkane to copper naphthenate.

In obtaining the data plotted on Figure 1, a series of tests was made in which gasoline was treated with various proportions of N,N'-disalicylal-1-2-diaminopropane and copper naphthenate. The various ratios of these treating materials are plotted as abscissa and the induction periods in minutes of the ASTM oxidation stability test are plotted as ordinates. Curve A is based on tests using one pound of copper naphthenate per thousand barrels of gasoline treated, curve B is based on five pounds of copper naphthenate per thousand barrels and curve C is based on 10 pounds of copper naphthenate per thousand barrels. It will be seen the three curves rise rapidly to a point represented by a ratio of 0.75:1. In plotting the data beyond this point it is best represented by a common curve D showing that increased ratios up to a ratio of 2:1 produced only a very slight increase in the induction period. It is shown, therefore, that the ratio of the salicylalamino alkane to copper naphthenate should be about 1:1 or at least as high as 0.75:1.

In Figure 2 the ratios of the N,N'-disalicylal-1-2-diaminopropane to copper naphthenate are plotted as abscissa and the ASTM gum in grams/100 cc. is plotted as ordinates. The data with the three different quantities of copper naphthenate (i. e. 1 lb., 5 lbs. and 10 lbs per 1000 bbls.) correspond so closely that they are represented by the single curve in the graph. It is shown that the point of minimum gum is approximately at the ratio of 0.75:1 and that higher ratios of the metal deactivator do not lower gum formation. Thus, from the standpoint of both induction period and gum it is shown that the ratio of the salicylalamino alkane to copper naphthenate should be about 1:1 or at least not lower than 0.75:1.

Cobalt naphthenate is very effective in the process. By way of example, a cracked naphtha was treated by adding cobalt naphthenate in a quantity equivalent to 10 lbs./1000 barrels of the naphtha, N,N'-disalicylal-1-2 diaminoproprane was added in a quantity equivalent to 5 lbs./1000 barrels and N,N' dialkyl-para-phenylene diamine was added in an amount equivalent to 10 lbs./1000 barrels. The naphtha after two hours standing was only very slightly positive to the doctor test and after standing overnight was completely negative. The combination of the cobalt naphthenate and the salicylalamino-alkane in the same quantities was found equally effective in treating a kerosene stock yielding upon overnight standing a product negative to the doctor test.

The organic salt dosage varies somewhat with the mercaptan content of the stock to be treated and also with the type of stock treated. Thus, for example, straight run stocks are somewhat more difficult to sweeten than cracked stocks containing olefins. In any case the quantity employed is much less than the stoichiometric quantity on the basis of the mercaptan content. Thus, in many cases, the amount of organic salt employed approximated $\frac{1}{10}$ of the stoichiometric. In typical operations quantities approximating 5 pounds per thousand barrels have been found adequate and in fact, increasing the quantity to 10 pounds per thousand barrels produced very little, if any, improvement. The sweetening reaction appears to be largely a catalytic reaction in which the paraphenylenediamine plays a part, that is, both the organic metallic salt and the paraphenylenediamine function in the sweetening reaction and the paraphenylenediamine stabilizes the product in storage. The time available for sweetening is also to be considered in deciding on the strength of organic metallic salt to be employed. Thus the holdup of stocks in tankage will vary from plant to plant.

Temperature is not particularly critical in the process although increasing the temperature from about 75° F. to about 100° F. caused a marked improvement in the rate of sweetening. Increasing the temperature above 100° F., however, did not appear to produce any increase in the rate of sweetening.

Air or oxygen blowing is not necessary for carrying out the process and, in fact, the process can be conducted satisfactorily in closed systems in which practically no air is present. However, air blowing has a tendency to increase somewhat the rate of sweetening.

The presence of traces of alkali metal hydroxide accelerates the rate of sweetening. Thus, for example, in treating a naphtha, having a mercaptan sulfur content of 0.019 gram per liter, with copper naphthenate, 10 lbs./1000 bbls. of naphtha, N,N' disalicylal-1-2-diamino-propane, 7.5 lbs./1000 bbls., and N,N' disecbutyl paraphenylenediamine, 5 lbs./1000 bbls., the mercaptan sulfur content in one days' standing was reduced to 0.008 gm./l., while with sodium hydroxide added in a quantity amounting to one milligram of 15° Baumé NaOH per quart, the mercaptan sulfur content in the same time of standing was reduced to 0.004. Thus, it is advantageous when employing the herein described process to completely sweeten and stabilize an oil previously subjected to a treatment with caustic, to avoid a complete removal of the caustic from the preceeding treat and permit traces of caustic to remain in the oil which is passed to the final sweetening and stabilizing treatment.

Although a preferred embodiment of the invention has been described herein, it will be understood that various changes and modifications may be made therein, while securing to a greater or less extent some or all of the benefits of the invention, without departing from the spirit and scope thereof.

We claim:

1. The method of treating hydrocarbon oils

containing mercaptan sulfur to effect simultaneous sweetening thereof and stabilization against oxidation that comprises contacting the oil with an organic metal salt, a paraphenylenediamine and an N-salicylalamino alkane to subject the oil to the combined action of said contacting materials.

2. The method of treating hydrocarbon oils containing mercaptan sulfur to effect simultaneous sweetening thereof and stabilization against oxidation that comprises contacting the oil with an organic copper salt, an N,N' dialkylparaphenylenediamine and a polysalicylalamino polyalkane to subject the oil to the combined action of said contacting materials.

3. The method of treating hydrocarbon oils containing mercaptan sulfur to effect simultaneous sweetening thereof and stabilization against oxidation that comprises contacting the oil with copper naphthenate, an N,N' dialkyl-paraphenylenediamine and a polysalicylalamino polyalkane to subject the oil to the combined action of said contacting materials.

4. The method of treating hydrocarbon oils containing mercaptan sulfur to effect simultaneous sweetening thereof and stabilization against oxidation that comprises contacting the oil with copper naphthenate, N,N' disecbutylparaphenylenediamine and N,N' - disalicylal-1-2-diaminopropane to subject the oil to the combined action of said contacting materials.

5. The method of treating hydrocarbon oils containing mercaptan sulfur to effect simultaneous sweetening thereof and stabilization against oxidation that comprises contacting the oil with cobalt naphthenate, an N,N' dialkylparaphenylenediamine and a polysalicylalamino polyalkane to subject the oil to the combined action of said contacting materials.

6. The method of treating hydrocarbon oils containing mercaptan sulfur to effect simultaneous sweetening thereof and stabilization against oxidation that comprises contacting the oil with cobalt naphthenate, N,N' disecbutyl-para-phenylenediamine and N,N' - disalicylal-1-2-diaminopropane to subject the oil to the combined action of said contacting materials.

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No references cited.