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PROCESS OF PRODUCING STABLE HYDROCARBON OILS

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This invention relates to the art of oil refining and more particularly to the treatment of light hydrocarbon oils having a tendency to discolor during storage and distribution such as certain types of gasoline, or motor fuel, and kerosene, to improve the color stability thereof.

An object of this invention is to provide an improved process of treating such substances in a convenient, efficient and economical manner.

A more specific object of this invention is to produce substantially colorless light hydrocarbon oils having an improved stability as to color and sedimentation so that they will remain colorless and clear, throughout an extended period of exposure to sunlight, air and moderately elevated temperatures such as are encountered commercially during storage and distribution.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties, and the relation of constituents, which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

The commonly accepted requirements of good commercial grades of gasoline and kerosene are that they shall not only be substantially colorless at the completion of the refining process, but that they shall remain colorless and clear throughout the somewhat extended period of storage which usually ensues prior to their sale to the ultimate consumer. During this interval certain of even the most carefully refined oils have heretofore frequently developed discoloration of a yellowish, pale orange, or more rarely, pinkish character, and this change has often been accompanied by the development of a cloudy appearance and formation of a deposit or sediment which is usually dark brown in color.

Such discoloration and sedimentation seriously depreciates the market value of such products, and in petroleum refinery practice, it is customary to test the refined gasoline and kerosene for stability by subjecting samples thereof in suitable receptacles to the action of sunlight, air, and moderate heat whereby the changes normally occurring during storage are accelerated. The oils which stand a test of exposure in colorless glass bottles to direct sunlight for several days or of heating for several hours to about 212° F., are considered to be of good quality, since experience has shown that they usually do not become discolored during storage.

This objectionable discoloration has been encountered more seriously with gasoline and kerosene manufactured by so-called "cracking processes" than with the similar oils obtained from crude petroleum by ordinary distillation and which are commonly known as "straight-run" products, although it is well recognized that gasolines and kerosenes which have been refined by any of the methods now in common use are likely to become discolored. Moreover since the causes of this color instability have not heretofore been understood, the attempts to overcome the difficulty have been varied in character and usually inefficient and costly of application. Examples of such attempts are the re-refining of such oils by filtering through fuller's earth, decolorizing charcoal and the like or redistillation of the oil usually with the aid of steam.

Straight run gasolines and kerosenes are sometimes refined by agitating with an alkaline solution of sodium plumbite, acid treatment being omitted. Gasolines treated in this way frequently become discolored, particularly if sulfur is added to the alkaline plumbite and gasoline mixture. In the case of kerosene it is common practice to filter the refined kerosene through fuller's earth, bauxite or other decolorizing agent to remove coloring matter. When freshly refined such gasolines and kerosenes are colorless and entirely free from traces of acid and alkali, but may rapidly become discolored during storage.

More frequently the practice of refining petroleum oils has included the well known steps of treatment with sulphuric acid, water,

alkali and "sweetening" agent and in the case of cracked gasolines the chemically treated gasoline or pressure distillate is redistilled. It is possible with proper cracking and rectifying apparatus, to produce a pressure distillate which has a boiling point range of ordinary gasoline, the chief objection to such practice has been the necessity of redistilling these oils after refining in order to obtain a color-stable product.

By the present invention, it has been found that the discoloration of hydrocarbon oils having a tendency to discolor during storage and distribution, such as certain gasolines and kerosenes, is effectively prevented by the addition of certain alkaline or basic substances to freshly prepared neutral oils as produced by the customary refining methods. It has long been recognized, in the refining of petroleum oils, that all traces of free mineral acids, such as sulphuric acid or sulphuric dioxide, used in the refining process, should be thoroughly removed by the above mentioned washing with water and neutralization with alkalies prior to the final distillation of the oil; the present invention is to be particularly distinguished from such old practice.

In the improved process of obtaining a color-stable product, comprising the present invention, it has been found desirable to commingle with the freshly prepared refined oil an alkaline or basic substance which will remain in the refined oil during storage and will effectively neutralize or overcome either any slight traces of acid which might be initially present therein after the last distillation and more particularly the acids which I find develop or tend to develop therein during such storage, it being preferred, however, to add the alkaline substance in amounts such that at the end of the storage period there is substantially no free excess of the alkaline agent. This discoloration is due perhaps to the presence in the refined oil of inorganic substances, such as free sulphur, or of organic substances of a more or less complex nature, which may yield acids by slow decomposition, oxidation or hydrolysis.

Although in the accomplishment of this result, alkaline substances of a relatively oil-insoluble nature such as hydrated lime, calcium carbonate and the like might be used, it has been found to be preferable to use oil-soluble bases such as ammonia or certain of its alkaline compounds or derivatives. Although ammonia is generally considered to be insoluble in mineral oils, it has been found that it is sufficiently soluble in light hydrocarbon oils to have the effect of preventing discoloration and that, although gasoline is capable of taking up or dissolving about 3 grams of anhydrous ammonia per gallon, at 20° C., usually 0.5 grams more or less of ammonia (NH_3), per gallon is sufficient to prevent discoloration or sedimentation on long standing or in the sunlight or heating tes

It has also been found that organic nitr gen bases or derivatives of ammonia, whi are generally more soluble in hydrocarb oils than gaseous ammonia, are also effecti in preventing discoloration. Of these ganic bases, it is preferred to employ th which do not readily form colored oxidati or condensation products such as benzy mine, trimethyl amine, ethylamine, popy mine and the aliphatic primary, seconda and tertiary amines generally. It has here fore been suggested to add amiline or oth aromatic amines to a refined hydrocarbon order to reduce "motor knock" and to eli nate the deposition of carbon in the combu tion chamber. Since these latter substanc tend readily to form colored oxidation a condensation products they are not suital for use to accomplish the purpose of the pr ent invention, and by the use of the term "c or-stable" in the present claims it is intend to exclude such substances.

It has been found that the present inve tion may be successfully applied to light h drocarbon oils such as gasoline and kerose having a tendency to discolor during stora and distribution, even when refined by any the methods now employed in refining su oils and that by the use of the principles the present invention it is possible in ma cases to simplify or curtail the series of op ations heretofore considered necessary. F example, it has been found in the case of t refining of cracked oils, that the final distill tion after the sulphuric acid, water, alka and "sweetening" treatment need not be ca ried out if a basic substance is added to t refined and neutralized oils, as describ above.

The following examples illustrate the ma ner and effectiveness of the application of t present invention to various types of gas line:

One-half gallon of crude cracked gasoli was refined by agitating with concentrat sulphuric acid in the proportions of fi pounds of acid per 42 gallons of oil, the ac and tar separated, the oil washed with wat and an excess of caustic soda and then swee ened by agitating with sodium plumbi solution. The gasoline thus refined was d vided into two portions, to one of which an monia was added in the proportions of abo 1.5 grams per gallon. Both the neutral po tion and the portion containing ammoni were then exposed to direct sunlight. Whi the color of the original refined gasoline wa 23 on the Saybolt color scale, the portio treated with ammonia retained this colo after two days' exposure to sunlight, the neu tralized oil containing no ammonia dark ened in color in three hours to about 15 o the Saybolt scale, and at the end of the tw days had become too dark to measure on th

aybolt scale and had formed a nearly black eposit of insoluble matter.

A straight run gasoline, distilled from a ude petroleum, was refined by sweetening ily, acid treatment being omitted, as is often ie practice with gasolines of this type. alf a gallon of this gasoline was sweetened y alkaline plumbite solution and a portion f the oil so refined was treated with amonia in the proportion of .6 gram per gallon; both portions were then exposed three ays to direct sunlight, at the end of which me the portion treated with ammonia owed a color of 25 on the Saybolt scale, ie same as the original color, and the porion containing no ammonia had become yelow in color equivalent to about 17 on the aybolt scale.

One half gallon of straight run gasoline as agitated with dilute calcium hypochlote solution until sweet to the alkaline plumite reaction. The product so treated was ivided into two portions, one of which was eated with ammonia in the proportions of .5 gram NH_3 per gallon of oil, and no furier treatment was given the other portion. oth samples showed 25+ color on the Sayolt scale but after two days' exposure to irect sunlight the one containing ammonia emained colorless but the one without amonia had become yellow in color to the exnt of about 19 on the Saybolt scale.

In practicing the invention on an industrial scale, it has been found to be convenient o prepare gaseous ammonia by adding conentrated aqueous ammonia to solid caustic lkali such as caustic soda, whereby nearly ry ammonia gas is evolved; quicklime may e used in the same way, but the ammonia s not so dry. The oil may be agitated with oncentrated aqueous ammonia and the aqueus layer, still containing most of the ammonia, then separated, but this is of course, vasteful of ammonia. A preferred procedure, adapted to treating large volumes of il, is to release gaseous ammonia from a ylinder of anhydrous ammonia, by means f a suitable reducing valve, and pass the mmonia gas at a controlled rate into the oil. he gas may be passed continuously into a tream of the oil as it passes to storage, or a arge tank of refined gasoline may be treated y bubbling the gas into the oil near the bottom.

When a liquid base such as trimethyl amine s employed, it is necessary merely to add a neasured quantity of the base to a definite olume of the oil in any way providing for roper mixing of the liquids. As with ammonia, the quantities required will depend omewhat upon the purity of the oil and upon ts tendency to discolor but the amounts ecessary to effect color-stability are within he range 0.5 to 5 grams per gallon for most amples of such oils; a very badly refined oil or one exceptionally rich in impurities, may require a somewhat larger amount.

Since certain changes in carrying out the above process, and certain modifications in the composition which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A process for stabilizing the color of gasoline, which comprises treating a freshly prepared and chemically refined gasoline with ammonia in an amount from about 0.5 grams to about 1.5 grams ammonia per gallon of gasoline treated.

2. A process for stabilizing the color of gasoline, which comprises treating a freshly prepared and chemically refined gasoline with ammonia in an amount of about 0.5 grams ammonia per gallon of gasoline treated.

In testimony whereof I affix my signature.

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