

## UNITED STATES PATENT OFFICE

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PROCESS FOR THE TREATMENT OF STORED  
CRACKED GASOLINEJacque C. Morrell, Chicago, Ill., assignor to Uni-  
versal Oil Products Company, Chicago, Ill., a  
corporation of DelawareNo Drawing. Application November 12, 1934,  
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1 Claim. (Cl. 196—43)

This invention relates more particularly to the treatment of unstable gasolines whose properties have deteriorated on storage due to oxidation, polymerization and other reactions among their constituents, the present application being a continuation in part of my earlier application Serial No. 406,514 filed Nov. 11, 1929.

It has been observed that when motor fuels or gasolines are stored, particularly cracked gasolines, and especially under the influence of light and oxygen, chemical changes occur which affect color, increase the gum formation, and reduce the anti-knock properties. The chemistry of these changes is somewhat obscure, although in practically all cases oxidation promotes these depreciating effects which occur upon storage. Cracked gasolines contain a relatively high percentage of unsaturated hydrocarbons, and it is believed that the changes which occur in the properties of the motor fuel during storage are related to chemical changes in these unsaturated hydrocarbons, especially in the more highly unsaturated groups, for example, the diolefins.

The formation of color in gasoline is undesirable because changes in color are usually accompanied by the formation of gum and tar-like substances which affect not only the sales value of the motor fuel, but also its performance in the operation of the motor, particularly in clogging up the gasoline feed lines, the moving parts of the carburetor and causing the sticking of valves in the motor. The development of more intense coloration is very undesirable from a sales standpoint as a small change in intensity makes a great difference in the appearance of gasoline in glass pump bowls.

The anti-knock property of a gasoline is among its most important and valuable characteristics which have a tendency to depreciate under average storage conditions in refineries. Knocking in a motor is evidenced by a pinging metallic sound which is accompanied by a reduction in the efficiency of the motor and in the mileage obtained per gallon of the fuel. The use of agents or kinds of motor fuel which prevent knocking adds to the efficiency of the motor and the motor fuel.

The rate at which different hydrocarbon motor fuels deteriorate on storage in respect to their valuable properties varies markedly with the chemical characteristics of the fuel which depend in turn upon the nature of the oil distilled or

cracked and the conditions of cracking in the case of cracked gasolines. The presence of relatively small quantities of nitrogen, sulfur and oxygen derivatives of hydrocarbons may also influence the rate of deterioration. In refinery practice it may be most economical to produce and store considerable quantities of motor fuel during the seasons when consumption of gasoline is low, so that it frequently happens that stocks are stored for abnormally long periods. In such cases considerable deterioration may ensue, particularly if the storage tanks are not full and there is considerable "breathing" in the vapor space above the oil. The present process comprises a method of treatment for restoring as far as possible the valuable properties of motor fuels which have been lost on storage.

In one specific embodiment the present invention comprises the treatment of materially deteriorated motor fuels with selected inorganic salts having a reducing action. The salts may be used either as solids or in solution.

A large amount of experimental and analytical work has shown the approximate course of the reactions which lead ultimately to the loss in color and anti-knock value and the increase in gums commonly observed in anti-knock motor fuels which have been stored for considerable periods of time. It is quite well established that the primary reaction which instigates the later changes consists in the addition of oxygen to olefins containing conjugated double bonds to form organic peroxides. At first the formation of these compounds is relatively slow but as they accumulate and their total percentage exceeds some definite value, the rate of formation is considerably accelerated so that the process becomes autocatalytic and not only hastens the formation of further quantities of peroxides but exerts a pronounced polymerizing effect upon olefins and other polymerizable compounds. In addition, there may be a more definite oxidizing action leading to the production of relatively stable compounds comprising aldehydes, alcohols, and acids in varying amounts. It has further been shown that the gums themselves which deposit from gasolines either on storage or during their carburetion and distribution in engine manifolds contain considerable quantities of peroxides. The presence of these peroxides in a motor fuel tends

to accelerate combustion and increase the knocking propensities of the fuel.

The restoration of properties, involving the substantially complete elimination of peroxides, the partial reduction of aldehydes, alcohols and acids and the depolymerization of high boiling polymers may be accomplished according to the present invention by treatment with solutions (generally aqueous) of various inorganic metal salts in which the metal exhibits its lower valence. In some cases the salts may be used in the solid form. This point will be discussed further in later paragraphs. Such salts are usually known as the "ous" salts and the different salts included in this category have the general property of absorbing oxygen or other elements and assuming a higher valence.

As examples of metals having reducing salts which are well known and as a rule easily available may be mentioned iron, tin, chromium, nickel, cobalt, cerium, copper, manganese, mercury and thallium. As a general rule, the use of salts of the commoner acids, such as the halogen acids and sulfuric acid will be preferable since these can be used with varying degrees of efficiency without having recourse to rarer and possibly more expensive compounds. The solubility of these reducing salts in water varies considerably and in the case of any one salt there will be an optimum concentration in water, a definite temperature and a definite volume of solution corresponding to most effective treatment. It is not intended to infer that salts which may be used alternatively have identical treating effects, this fact being more or less obvious to chemists.

Other groups of reducing salts which may be used within the concepts of the present invention include certain arsenites, antimonites and phosphites, usually of the alkali metals since these have sufficient solubility in water at ordinary temperatures to make possible the use of treating solutions of good efficiency. It is within the scope of the invention also to use ferrocyanides in case their solubility in water is great enough.

The operations of treatment for restoring properties of deteriorated gasolines by the present process are relatively simple and when solutions of salts are used may be conducted in the same general types of equipment as are ordinarily employed in treating oils with liquid reagents such as sulfuric acid, caustic soda and sweetening and washing solutions. For example, a solution of a reducing salt may be agitated with a deteriorated gasoline in the ordinary type of batch agitator using mechanical stirring devices or circulation from the bottom of the agitator back into the top by means of outside force pumps. The solutions may also be used in continuous treating plants consisting of a series of connected units each comprising a mixer followed by a settling tank from the bottom of which spent or partly spent aqueous reagents are drawn and the treated liquids are discharged from the top. In other words, the process is not limited to the use of any particular type of mechanical equipment.

As an alternative mode of procedure it may sometimes be convenient and practical to effect the desired reducing treatments using finely divided solid salts. In such cases the solid may be agitated with the gasoline to be treated either at ordinary or elevated temperatures (using refluxing or increased pressures to prevent loss of light constituents), or the gasoline may be filtered through granular beds of reducing salts. Each

of these alternative methods of operation have their advantages in individual cases and may be employed as desired.

The present process may also be employed in conjunction with any other treatments which may be considered necessary or of advantage in bringing aged stocks back as nearly as possible to their original values. Analytical data indicate that the principal action of reducing agents of the present character on stored distillates is to "deoxidize" the same, to eliminate peroxides and to some extent the compounds in which the oxygen is in more stable combination such as the aldehydes, alcohols and acids already mentioned. It is seldom possible to depolymerize to any great extent and in case gummy or resinous materials have been formed in relatively large amounts, redistillation following the treatments will be necessary, in which step the materials boiling above the desired end point of the finished gasoline remain as a heavy reflux in the fractionator.

It is a feature of the present invention that its greatest value lies in its application to unstable gasoline stocks which have suffered more or less serious deterioration in their properties. Laboratory tests have indicated that extensive changes seldom occur when the peroxide content of a gasoline is about 0.5 or less, measured as mgs. of available oxygen per liter of sample. Beyond this point extensive changes occur which follow the previously indicated mechanism. When large amounts of peroxides have been formed with the accompanying gums, aldehydes, et cetera, it has been found that further depreciation of gasolines cannot be prevented by the use of ordinary inhibitors since these are ineffective in the presence of the relatively large amounts of reactive oxygen. Since the amount of inhibitor which may be used is limited by such considerations as the cost of the material, the residue formed on evaporation, possible color effects, et cetera, the present process offers a definite supplementary treatment which renders stocks otherwise not susceptible to inhibition capable of proper response.

The following examples are given to indicate the general character of treating effects obtainable in the practical application of the present process and while they are illustrative they are selected from a considerable number and they are not given with the intent of limiting the scope of the invention to the specific instances presented:

#### Example I

A deteriorated cracked gasoline was treated by agitation at ordinary temperatures with granular ferrous chloride used in an amount of about 1% of the weight of the gasoline. The significant properties of the gasoline before and after this treatment are given in the following table:

| Property        | Before treatment | After treatment |
|-----------------|------------------|-----------------|
| Peroxide number | 5.4              | 1.0             |
| Color, Saybolt  | Light yellow     | 25              |
| Octane number   | 40               | 60              |

#### Example II

The same gasoline as in Example I was treated with solid cuprous chloride. In this case it was found that after agitation for about 24 hours at ordinary temperatures that the peroxide number

was substantially zero while the color and anti-knock value had been restored the same as in Example I.

#### Example III

5 A Mid-Continent cracked gasoline which had been stored for a considerable time was found to have deteriorated considerably in respect to gum content, anti-knock value and color. It 10 had a peroxide number of 6.3. This deteriorated gasoline was treated at ordinary temperatures with about 10% by volume of a saturated solution of ferrous sulfate. The significant properties before and after treatment are again given 15 in the following table:

| Properties              | Before treatment | After treatment |
|-------------------------|------------------|-----------------|
| 20 Peroxide number..... | 6.3              | 1.1             |
| Color, Saybolt.....     | Yellow           | 20              |
| Octane number.....      | 45               | 61              |

#### Example IV

25 In this case the same deteriorated gasoline used in Example III was treated with about 5% by volume of a saturated solution of stannous chloride which contained no stannic salt. The re-

sults of this treatment are again tabulated below:

| Properties           | Before treatment | After treatment |
|----------------------|------------------|-----------------|
| Peroxide number..... | 6.3              | 0.60            |
| Color, Saybolt.....  | Yellow           | 24              |
| Octane number.....   | 45               | 62              |

10 The features and advantages of the present process are obvious from a consideration of the preceding specification and numerical data presented, although neither section should be construed as imposing undue limitations upon the invention's generally broad scope. 15

I claim as my invention:

A process for restoring deteriorated cracked gasoline containing organic peroxides developed therein as a characteristic of the deterioration and tending to form gums and to reduce the anti-knock value characteristic of the gasoline before its said deterioration, said process comprising treating said deteriorated cracked gasoline with a ferrous salt having a reducing action on said peroxides, and separating any unconsumed quantity of said salt and the reaction products from the thus treated gasoline. 20 25

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