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UNITED STATES PATENT OFFICE.

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ART OF IMPROVING MINERAL OILS.

No Drawing.

Application filed March 15, 1923. Serial No. 625,262.

This invention relates to art of improving mineral oils; and it relates more particularly to the treatment of oils such as petroleum, petroleum distillates and residua, in the manufacture of valuable commercial products.

While the invention is considered to be of broad scope in its general applicability to mineral oils of widely divergent characteristics and for the manufacture of various products, its most important commercial application at the present time is in the treatment of relatively light petroleum distillates having specific gravities of from about .730 to .830, and distillation ranges lying between about 100° and 600° F., particularly motor fuels, such as gasolines and other motor fuels of this general type, as well as kerosenes, for increasing stability thereof and otherwise improving the same. Accordingly this phase of the matter will be more especially emphasized and described in detail hereinafter.

It is common knowledge that commercial gasolines or other motor fuels heretofore available are unstable, especially those made by cracking processes; that is, they undergo substantial changes in composition in a comparatively short time under storage conditions, these changes being highly undesirable and prejudicial to attainment of best results in utilizing the fuel. While more or less obscure as to exact chemical character, these changes are known to result in the formation of compounds in the gasoline or other motor fuel which, upon evaporation of the motor fuel, manifest themselves in the form of a more or less gummy or resinous residue. In the case of some motor fuels, this resinous or gummy formation occurs to such an extent that, even without evaporation, an insoluble residue of said material is deposited upon the bottom of a container in which the motor fuel is stored. In all cases, however, whether deposition of the gummy material occurs before evaporation or not, the necessary potential constituents thereof are present in ordinary commercial motor fuels which can be shown by test soon after final distillation. This tendency is usually more pronounced in the case of motor fuels obtained from the various cracking processes, which fuels are characterized by a substantial content of unsaturates. However, the extent to which the undesirable gummy or resinous compounds are formed does not appear to bear any simple or direct relation

to the quantity of unsaturates present in a given motor fuel; and this formation of gummy or resinous compounds, or instability, is characteristic of commercial straight-run gasolines as well as gasolines produced by cracking.

It is generally believed that the instability above referred to is due at least largely to polymerization of certain constituents invariably present in gasolines or other motor fuels as commercially produced heretofore, this polymerization beginning very soon after distillation and progressing usually rather slowly at a rate depending upon the character of the particular motor fuel in question and the conditions of its storage. Sometimes part of the final polymerization products separate out, but the greater part remain in solution. The practical effect of this polymerization is that upon evaporation the resultant gummy polymers which then separate foul the carburetors and valves of internal combustion engines in which the fuel is used, cause excessive carbonizing, and are otherwise seriously objectionable.

A successful method of stabilizing motor fuels and the like by freeing the same of polymerizable constituents is described and claimed in the application of William G. Leamon, Serial No. 621,076, filed February 24, 1923, said method comprising the treatment of the motor fuel or other mineral oil with a solution of a polymerizing agent in a solvent that is miscible with or soluble in the oil to be treated. Specifically, said application describes the employment of anhydrous aluminum chlorid dissolved in ether for the purposes stated.

The present applicant has discovered that excellent results can be obtained by using glacial acetic acid in place of aluminum chlorid, the effectiveness of glacial acetic acid being practically as marked as that of aluminum chlorid, and its behavior being in some respects more advantageous as will more fully hereinafter appear. Glacial acetic acid alone, without ether or other solvent, has been found by the present applicant to have a specific polymerizing action that can be utilized in practice to effect the desired modifying or stabilizing action; but such action is distinctly more dependable and complete if a suitable solvent, especially ether (ethyl ether), is employed in mixture with the glacial acetic acid. Whether this

is due simply to the distributing action of the solvent or to some chemical action in the nature of formation of complexes with the polymerizable constituents present in the oil undergoing treatment, this applicant does not undertake to say, but is content to note the fact that the presence of the ether or other suitable solvent in mixture with glacial acetic acid does produce a distinctly more advantageous result.

In order to explain more fully the principles underlying the invention, the stabilization of a motor fuel or gasoline in accordance with the novel process will be described in detail as illustrating a practical application of the invention in one of its most advantageous forms. In this specific example it will be assumed that the motor fuel to be stabilized is a crude motor fuel obtained by a cracking process and containing a large percentage of unsaturates, say as much as 30 or 40 per cent. In treating such a crude motor fuel, it is subjected to the action of a small percentage of glacial acetic acid which, in a typical instance, may be around 0.15 per cent. It may be stated generally that the amount of glacial acetic acid need never exceed 1 per cent of the weight of the oil to be treated. While, as already stated, it is possible to effect the treatment without the employment of a solvent in conjunction with the glacial acetic acid, it is much more desirable to use a solvent; and where the solvent is ether, a mixture consisting of four volumes of glacial acetic acid and three volumes of ether is found to work well. Assuming the use of such a mixture, a sufficient quantity thereof to represent the necessary small percentage of glacial acetic acid is added to the crude motor fuel and mixed therewith, with the aid of agitation or otherwise, at ordinary room temperature. After standing for some little time, say an hour or so in a typical instance, the color of the treated motor fuel is found to darken perceptibly, which indicates that the polymerizing action has proceeded to completion or at least so far that further treatment for removal of the polymerized products may follow immediately, and in fact should follow fairly promptly in order to obtain the best results. Accordingly the motor fuel is next distilled in an ordinary distillation apparatus such as may be used for re-running crude motor fuel. No special precautions are necessary during the distillation except that care should be taken not to carry the distillation so far as to reduce the volume of liquid in the still to a point where overheating and breaking down of the polymers in the residue would take place to a substantial extent. In a typical crude motor fuel, it is usually possible to distill over from 80 to 90 per cent of the original volume after treatment with

the glacial acetic acid as described. The distillate obtained is a high grade motor fuel or gasoline that is stable. The residue in the still is an oily material; and where the conditions and extent of distillation are parallel, it is notably more limpid than where aluminum chloride is used as the polymerizing and stabilizing agent. Furthermore, when glacial acetic acid is used, no by-products are formed that attack the distilling apparatus. These are practical advantages of considerable importance in commercial work. If desired, the slight trace of free acetic acid present in the treated motor fuel undergoing distillation may be neutralized either by introducing a suitable neutralizing agent such as sodium bicarbonate into the material in the still, or by causing the vapors to pass through lime or other neutralizing material on their way to the condenser. It is also feasible, of course, to wash the condensed distillate with water or a slightly alkaline solution to remove any free acetic acid present.

Instead of adding the ether solution of glacial acetic acid to the crude motor fuel and commingling it therewith in the cold, it is also feasible to effect this treatment at a somewhat higher temperature, say 100° C. This somewhat increases the rapidity of the polymerizing action but ordinarily does not offer sufficient advantages to make it preferable over treatment at ordinary room temperature. A particular advantage attained by using glacial acetic acid in place of aluminum chlorid resides in the fact that although the polymerizing action of glacial acetic acid is amply rapid for all practical purposes, it is somewhat slower and more gradual than the action of aluminum chlorid and is therefore less likely to go too far and break down polymerized products once these have been formed. In other words, since the action of glacial acetic acid is slower and more gradual, the most favorable time for effecting separation of the polymerized constituents after treatment with the polymerizing agent can be more readily availed of in practice. Thus, as pointed out above, where the present process is carried out at ordinary room temperature, something like an hour usually elapses between the addition of the polymerizing agent and the completion of the polymerizing reaction to such an extent that separation of the polymers may be satisfactorily effected, and even if the mixture be allowed to stand for a considerable time thereafter the further action of the glacial acetic acid does not progress to a harmful extent. In the case of aluminum chlorid, on the other hand, if the treated solution be allowed to stand much longer than twenty-four hours before distillation, it is found that in some cases the aluminum chlorid has acted to break down some of the

polymers previously formed and as a result the distillate finally obtained under these circumstances is not entirely stable.

What I claim is:

5 1. The process of removing polymerizable constituents from mineral oils which comprises subjecting such mineral oil to the action of a solution of glacial acetic acid in ether, and separating resultant polymerized
0 products.

2. The process of removing polymerizable constituents from mineral oils which comprises subjecting such mineral oil to the action of a solution of glacial acetic acid in ether, and separating resultant polymerized
5 products, the quantity of glacial acetic acid used being less than one per cent by weight of said oil.

3. The process of improving gasoline or
10 other motor fuel distillate which comprises commingling therewith a mixture of glacial acetic acid with ethyl ether at a temperature favorable to polymerization of polymerizable constituents present in said motor fuel but
15 insufficiently high to effect substantial break-

ing down or cracking, and separating resultant polymerized products, the quantity of glacial acetic acid used being less than one per cent of the distillate treated.

4. The process of producing a stable motor
30 fuel which comprises subjecting a crude motor fuel resulting from heat treatment of mineral oil and containing up to about forty per cent of unsaturates to the polymerizing
35 action of glacial acetic acid employed in quantity not exceeding one per cent of the weight of the said fuel treated, and distilling a substantially stable motor fuel product from the crude motor fuel thus treated.

5. The process as defined in claim 4, further
40 characterized by the fact that the quantity of glacial acetic acid employed is approximately 0.15 per cent of the weight of fuel treated.

6. The process as defined in claim 4, further characterized by the fact that the acetic
acid employed is dissolved in ethyl ether.

In testimony whereof I hereunto affix my signature.

FORREST WAYLAND ELEY.