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STABILIZED KEROSENE

Amiot P. Hewlett, Westfield, and Gerald E. Phillips, Cranford, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

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This invention relates to the color stabilization of refined minerals of the kerosene boiling range which are intended to be used as range oils and the like.

Considerable difficulty in the past has been occasioned by the fact that refined oils of the type in question "go off color" i. e., become darker in color, during storage or shipment involving substantial periods of time, particularly in warm weather and in hot climates. This is particularly true when these products are cased in small metal cans.

Although this discolorization may be reduced substantially in some cases by washing out all traces of $ZnCl_2$, $FeCl_3$ or other soldering flux which was used in the manufacture of the cans, yet this procedure is both laborious and expensive and it is an object of the present invention to stabilize the color of such cased white products by a very simple and economic method.

Broadly, the invention consists in incorporating in the refined oil before storage or shipment a small amount of a suitable stabilizing agent belonging to the class of chemical compounds known as ketones. Acetone, which may also be called methyl-methyl ketone or dimethyl ketone, is the simplest member of this class and has been found very effective as a color stabilizer according to the purview of this invention.

The type of refined oils intended to come within the scope of this invention includes petroleum distillates of approximately the kerosene boiling range, i. e., approximately 300° F. to 600° F., having flash point not lower than about 100° F. having a color suitable for marketing, whether these oils are untreated or whether they have been prepared by some decolorizing treatment such as clay treating, acid treating, and the like. These products may have been subjected to any of the other refining steps such as soda washing, sweetening, etc., which are commonly used in the art for finishing such oils. These refined oils are used particularly for burning in lamps and ranges and a water white color is generally considered an indication of an oil which has satisfactory burning qualities. For example, U. S. Government specifications for kerosene call for a Saybolt color not lower than 16 while for "long time burning oil" the minimum color is 21.

In an attempt to predict the tendency of a refined oil to become discolored during storage the so-called "color hold test" has been used; this involves inspection of the color after heating a sample of the oil for 16 hours at 212° F. Although sometimes there is a fair correlation between the color hold test and the actual storage stability as measured by inspection of the color periodically during actual storage of samples of suitable size, for instance, one gallon cans, yet in many cases the color hold test is not a satisfactory basis for predicting the storage stability.

A comparison of these two tests as applied to a number of other refined oils is shown in the following Table 1.

TABLE 1

Refined oil	Color	Color hold 16 hrs. @ 212°	Color drop	Storage stability	
				Months storage	Color after specified months storage
Refined oil 1 from source A	+26	+26	No	18	+19.
Refined oil 2 from source A	+23	+22	1	12	+20.
Refined oil 3 from source A	+22	+21	1	12	+18.
Refined oil from source B	+21	+18	3	15–18	Straw.
Kerosene from source C	+24	+21	3	6	Straw.
Kerosene from source D	+26	+17	9	9	Straw.

The present invention should not be confused with the use of anti-oxidants for petroleum oils, such as gum inhibitors in gasoline, etc., for it has been found that a number of substances which have definite values as gum inhibitors in gasoline, for example, tricresol, or light stabilizers for gasoline, for example, naphthalene, and butyl amines, distinctly accelerate color loss in refined oils such as kerosene and the like.

In carrying out the present invention only a relatively small amount of stabilizer is required, for instance, between the approximate limits of 1 to 10 cc. per gallon of refined oil. 10 cc. per gallon corresponds approximately to 0.25% by volume. Although the amount required to produce the best results with the least cost will vary to a certain extent according to the source of crude from which the refined oil was prepared and will depend upon the refining steps to which it had been subjected as well as the severity of the conditions, i. e., temperature, time, etc., under which it is intended to be stabilized, generally about 3 cc. of stabilizer per gallon of oil is sufficient.

Although acetone is referred to herein as the preferred stabilizer, other ketones, particularly those of relatively low molecular weight and sufficient oil solubility, may be used, for instance, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, diisopropyl ketone, methyl phenyl ketone, quinone, etc. Although acetone is sufficiently soluble in refined oils for the purpose in question it may be desirable to use a small amount of a mutual solvent for some of the less soluble ketones.

Having thus described the general principles of the invention some experimental data are given

herewith for the sake of illustration and in order to point out the advantages of the invention. Table 2 shows the effect of several commercial antioxidants on the color stability of a kerosene from source C, the original inspection of which showed a color of +24, color hold +21 and mercury No. 7.

TABLE 2

Material added	Stability trend on storage in gallon cans* (color after the following month's storage)				
	0	1	2	3	6
Blank	+24	+23	+18	+5	(**)
Do	+24	+23	+17	+11	Straw.
Commercial anti-oxidant No. 1	+24	+15	−10	Straw	Cans badly corroded.
Do	+24	+16	−2	do	Do.
Commercial anti-oxidant No. 2	+28	+27	+18	−2	Straw.
Do	+28	+27	+19	+14	−12.
Commercial anti-oxidant No. 3	+24	+20	+15	Straw	
Do	+24	+18	+10	do	
Commercial anti-oxidant No. 4	+24	+19	+14	do	
Do	+24	+18	+8	do	

*Samples were stored in a room in which the temperature was raised and thermostatically controlled at 100° F. during the day and allowed to cool during the night.

**Removed for can inspection.

The data in Table 2 show that the various commercial anti-oxidants tested failed to improve the color stability of the kerosene used and, in fact, several of the addition agents actually accelerated the loss of color.

In the following table data are given showing the effect of acetone on the color stability of sweetened water white kerosene, the original inspection of which showed a color of +26, color hold +26, and mercury No. 4.

For the sake of comparison some tests are also included on hydroquinone in acetone solution and in alcohol solution.

TABLE 3

Material added (quantity per gallon)	Stability trend on storage in gallon cans* (color after the following month's storage)							
	0	1	3	6	9	12	15	18
Blank	+26	+22	+21	+17	+20	+21	+20	+19
Do	+26	+23	+22	+22	+21	+20	+20	+19
Acetone (3 cc.)	+26	+26	+25	+24	+22	+22	+22	+21
Do	+26	+24	+24	+24	+22	+23	+24	+23
Hydroquinone (60 mg.) acetone sol	+26	+22	+22	+19	+18	+19	+19	+16
Do	+26	+22	+21	+20	+17	+18	+19	+15
Hydroquinone (60 mg.) alcohol sol	+26	+21	+19	+16	+13	+13	+13	+8
Do	+26	+22	+21	+18	+16	+16	+16	+1

*Same conditions as in Table 2.

The data in the above Table 3 might be summarized as follows:

Stabilizer	Color drop after 18 mos. storage (average of two samples)
Blank	7
Acetone (3 cc.)	4
Hydroquinone (60 mg.) in acetone	10.5
Hydroquinone (60 mg.) in alcohol	21.5

In other words acetone reduced the 18 months storage color loss from 7 to 4 while the hydroquinone increased the color loss both when dissolved in acetone and in alcohol.

Inasmuch as a large quantity of refined oil is exported from this country into foreign countries and considerable trouble results from the shipment of such refined oils into countries situated in hot climates, a number of cases of refined oil from source A were actually shipped from the United States to Dutch Guiana (where the average yearly temperature is much warmer than in New York, for example), stored there for 14 months and then inspected after return shipment to the United States. In this series of tests various stabilizers were added, always leaving a blank sample in the same case, and ten cases being tested for each stabilizer.

TABLE 4

Export storage tests

ORIGINAL INSPECTION OF REFINED OIL USED

	Cases numbered	
	1–5	6–10
Color	+22	+23
Color hold (212)	+21	+21
Hg#	6	6
Ring No.	54	54

COLOR OF SAMPLES AFTER SHIPPING AND RETURN

Case No.	Series A		Series B		Series C	
	Stabilizer* blank	Acetone	Blank	Tri-n-butyl amine	Blank	Commercial anti-oxidant No. 2
1	Straw	+19	+17	Straw	+3	−5
2	−1	+22	+21	do	+19	−9
3	−5	+21	+22	+2	+9	+6
4	+1	+21	−11	Straw	+20	−13
5	−0	+21	+10	do	+16	+6
Aver. 1–5	Below −1	+21	+12	Straw	+13	−3
6	+17	+21	+18	Straw	+17	Straw
7	+18	+22	+1	−13	+5	−9
8	+17	+22	+16	Straw	+15	+16
9	+20	+22	+17	do	+18	+11
10	+19	+21	+18	do	+10	+2
Aver. 6–10	+18	+22	+14	Straw	+13	Below +4

*Amounts of stabilizers used:

Acetone	14 cc/5 gal.
Tri-n-butyl amine	0.8 lb./1000 gal.
Commercial anti-oxidant No. 2	0.8 lb./1000 gal.

The above Table 4 shows that acetone successfully maintained a color +21 or +22 substantially the same as the original color (+22 or +23) whereas the blank samples in cases 1 to 5 had dropped to an average color less than −1 and those in cases 6 to 10 had dropped to an average color of about +18.

Table 4 also shows that tri-normal-butyl amine and commercial anti-oxidant #2 both accelerated the color loss.

Results of tests to determine the effect of the added acetone on the burning quality of refined oil are shown in the following table:

TABLE 5

	Refined oil	Refined oil+3 cc. acetone per gallon
Gravity	46.6	46.6.
Refined oil viscosity	355	355.
Consumption—(fluid ounces burned 8 hours):		
1	16.0	15.5.
2	15.6	15.3.
3	15.7	15.5.
Remarks:		
Wick	Not excessive soft, dull, slightly disintegrated.	Not excessive soft, dull, slightly disintegrated.
Flame	Shape satisfactory	Shape satisfactory.
Burning quality	Satisfactory	Satisfactory.

Table 5 shows that the acetone had no appreciable effect on the burning quality of the refined oil (kerosene) tested.

Thus the unexpected improvement in stability of the refined oils is obtained without any attendant deleterious effects.

It is not intended that this invention be limited to the specific examples which are given here only for the sake of illustration, nor to any theory as to the operation of the invention, but only by the appended claims in which it is intended to claim all novelty inherent in this invention as broadly as the prior art permits.

We claim:

1. A stabilized refined oil consisting of a petroleum distillate having a boiling point range of from about 300° to about 600° F. and having a flash point of more than 100° F., and a lower aliphatic ketone in an amount between about .025% and about 0.25% by volume of the petroleum distillate.

2. A composition as in claim 1 wherein the lower aliphatic ketone is acetone.

3. A composition as in claim 1 wherein the lower aliphatic ketone is acetone present in an amount of about .08% by volume of the petroleum distillate.

4. The stabilized product consisting of kerosene having a boiling point range of from about 300° F. to about 600° F. and between about .025% and about 0.25% by volume of acetone, the mixture being cased in metal containers.

5. The method of stabilizing a petroleum distillate having a boiling point range of from about 300° to about 600° F. and having a flash point of more than 100° F. which consists in adding to said distillate between about .025% and about 0.25% by volume of a lower aliphatic ketone.

6. Process as in claim 5 wherein the lower aliphatic ketone is acetone.

7. Process as in claim 5 wherein the lower aliphatic ketone is acetone used in an amount of about .08% by volume of the petroleum distillate.

8. The method of stabilizing a petroleum distillate having a boiling point range of from about 300° to about 600° F. and having a flash point of more than 100° F. and which is cased in metal containers which consists in adding between about 1 cc. and about 10 cc. of a lower aliphatic ketone per gallon of petroleum distillate.

9. The process as in claim 8 wherein the lower aliphatic ketone is acetone.

10. The process as in claim 8 wherein the lower aliphatic ketone is acetone and used in an amount of about .08% by volume of the petroleum distillate.

AMIOT P. HEWLETT.
GERALD E. PHILLIPS.