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METHOD OF STABILIZING CARBONYL
CONTAINING MOTOR FUELSRichmond T. Bell, Deerfield, Ill., assignor to The
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of OhioNo Drawing. Application October 15, 1941,
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18 Claims. (Cl. 44-66)

This invention relates to a method of stabilizing against loss in octane value, motor fuel to which has been added metal carbonyl compounds, and to the stabilized motor fuel.

It is known that various metal carbonyls such as iron, cobalt and nickel pentacarbonyl, iron tetracarbonyl, iron and cobalt tricarbonyl mercaptide and various metal nitrosyl carbonyls improve the antiknock characteristics of hydrocarbon motor fuels. However, the various metal carbonyl compounds are unstable, decomposing in the presence of air and/or light with the formation of heavy precipitates and resultant loss of octane value of the motor fuel. Although I have discovered that metal tricarbonyl mercaptides are more stable than the metal carbonyls, even the mercaptides decompose upon storage when exposed to daylight and air for a sufficient period of time.

I have discovered that hydrocarbon motor fuels which contain metal carbonyl compounds can be stabilized against deterioration and decomposition by incorporating in the motor fuel phosphatides such as lecithin and cephalin.

In accordance with my invention the phosphatide may be added to the motor fuel either before, together with or after the addition of the metal carbonyl compound, but I prefer to have the phosphatide present in the motor fuel at the time the carbonyl is added, particularly in those cases where the motor fuel contains mercaptans and a polymeric carbonyl such as iron tetracarbonyl, capable of reacting with the mercaptans to form iron tricarbonyl mercaptide, is added.

In my co-pending application Serial No. 385,869 I have disclosed and claimed a method for increasing antiknock of motor fuels and for sweetening mercaptan-containing motor fuels by adding thereto iron or cobalt tetracarbonyl. At temperatures of approximately 160°-200° F. the tetracarbonyl readily reacts with the mercaptans to form the tricarbonyl mercaptide. Although the resulting motor fuel has greatly improved antiknock, the process is attendant with certain disadvantages. Upon reaction of the mercaptans in the motor fuel with the tetracarbonyl, a light precipitate forms which is composed chiefly of iron oxide with small amounts of other iron compounds. This precipitate must be separated from the motor fuel before using. Moreover, the

motor fuel upon storage in the daylight exposed to air slowly deteriorates. A series of samples were prepared in some of which iron tricarbonyl phenyl mercaptide was added to sweet straight run petroleum naphtha having an octane number of 50 and in some of which iron tetracarbonyl was added to sour gasoline having an octane of 61.9 and prepared by blending gasoline from high pressure thermal cracking of petroleum oil and straight run gasoline, and the mixture heated to 170°-180° for a period of thirty minutes to one hour. These samples were permitted to stand in glass bottles exposed to daylight at room temperature with an air space in the top of the bottle. The following results were obtained:

Table I

Compound in solution	Iron, g./gal.	Original octane number	Days in storage	Appearance	Octane number after storage
Fe(CO) ₅ SC ₆ H ₅	0.9	53.4	56	Large, flocculent precipitate.	51.0
Do	1.8	54.8	56	do	52.5
Do	3.6	56.2	56	do	54.1
Fe(CO) ₅ SR ¹	0.4	63.6	56	do	61.4
Do	0.9	65.7	56	do	62.9
Do	2.3	68.2	56	do	65.3

¹ R may be any alkyl or aryl radical.

A sample of the same sour gasoline was sweetened with iron tetracarbonyl in the same manner as previously described except that 2.3 grams of lecithin per gallon of gasoline was dissolved therein before introduction of the iron tetracarbonyl. The reaction appeared to proceed in the same manner as it did without the lecithin. The dark green color of the iron tetracarbonyl in solution changed to dark red, but the resulting motor fuel was clear and free of any precipitate. It was observed that the color of the motor fuel was a somewhat darker red than that obtained without the presence of lecithin. The resulting gasoline had an octane number of 68 as compared with 68.2 obtained when the gasoline was sweetened without the presence of lecithin. The same amount of iron tetracarbonyl was required to sweeten the gasoline with and without the presence of lecithin. This amount was found to be 7 grams or the equivalent of 2.3 grams of iron per

gallon of gasoline. Thus, by sweetening in the presence of the phosphatide, loss of iron and the necessity of filtering the gasoline are avoided.

In order to demonstrate the relative stability of motor fuel made with and without the presence of lecithin, a number of samples were prepared and the samples were observed daily over a period of 26 days. The following results were obtained:

ing of the motor fuel and a phosphatide in an amount at least approximately equal in weight to the metal present as carbonyl compound.

2. A motor fuel in accordance with claim 1 in which the phosphatide is lecithin.

3. A motor fuel in accordance with claim 1 in which the phosphatide is cephalin.

4. A motor fuel in accordance with claim 1 in

Table II

Sample	Identification	Time of cloud and precipitate formation, days					
		Precipitate during reaction	Solution		Precipitate		
			Clear for	Cloudy after	Slight after	Appreciable after	Large after
1-----	Gasoline sweetened by addition of 7 g. $\text{Fe}_3(\text{CO})_{12}$ and filtered. No lecithin present.	Appreciable.	$\frac{1}{4}$	$\frac{1}{2}$	1	$1\frac{1}{2}$	3
2-----	Sample 1+16# lecithin/1,000 bbls.	do	$\frac{1}{2}$	1	1	2	4
3-----	Sample 1+16# lecithin/1,000 bbls+16# isobutyl p-aminophenol/1,000 bbls.	do	$\frac{1}{2}$	1	2	3	6
4-----	Gasoline sweetened by addition of 7 g. $\text{Fe}_3(\text{CO})_{12}$ with 213# lecithin/1,000 bbls. present during reaction.	None	26	-----	-----	-----	-----
5-----	Sample 4+16# isobutyl p-aminophenol/1,000 bbls.	do	11	-----	-----	10	11
6-----	Gasoline sweetened by addition of 7 g. $\text{Fe}_3(\text{CO})_{12}$. 213 #lecithin/1,000 bbls. added after reaction but before filtration.	Appreciable.	26	-----	-----	-----	-----

It will be seen from Table II that the addition of lecithin in the amount of 16 pounds per 1000 barrels of gasoline had no appreciable effect on the stability of the motor fuel, but that upon addition of larger quantities of lecithin the stability was markedly improved as shown by the fact that it remained clear for a period of 26 days. The addition of a well known gum inhibitor—namely, isobutyl p-aminophenol—in quantities commonly added to gasoline was harmful in that it detracted from the stability of the motor fuel, as shown by a comparison of samples 4 and 5. It will also be noted from the results tabulated in Table II that by having the lecithin present in the gasoline during the reaction between the iron tetracarbonyl and the mercaptans, precipitation was avoided during reaction, whereas where the lecithin was not added until after the reaction, an appreciable precipitate formed. The stability of the resulting motor fuel in both cases was the same.

Stability tests were also made on iron pentacarbonyl and it was found that the effect of lecithin in stabilizing motor fuel containing this material was similar to its effect in connection with iron tricarbonyl mercaptide, but the stability of the fuel was not as great as in the case of the mercaptide compound.

As previously shown, small amounts of lecithin—that is, amounts comparable to amounts of inhibitors which are commonly added to motor fuel—have substantially no effect in inhibiting deterioration of the carbonyl compounds. I have found that lecithin or other phosphatide should be added in amounts approximately .50 to 10 grams per gallon of motor fuel and preferably in amounts approximately corresponding to the amount of iron contained in the carbonyl compound added to the motor fuel, in order to get sufficient stability for commercial purposes. Larger amounts of lecithin will give increased stability and smaller amounts will give decreased stability.

I claim:

1. A motor fuel comprising a major portion of hydrocarbons boiling within the gasoline boiling range, a minor but sufficient amount of a metal carbonyl compound to raise the anti-knock rat-

which the metal carbonyl compound is an iron compound.

5. A motor fuel comprising a major portion of hydrocarbons boiling within the gasoline boiling range, a minor but sufficient amount of metal tricarbonyl mercaptide to raise the anti-knock rating of the motor fuel and a phosphatide in an amount at least approximately equal in weight to the metal present as tricarbonyl mercaptide.

6. A motor fuel in accordance with claim 5 in which the metal tricarbonyl mercaptide is cobalt tricarbonyl mercaptide.

7. A motor fuel in accordance with claim 5 in which the phosphatide is lecithin.

8. A motor fuel in accordance with claim 5 in which the phosphatide is cephalin.

9. A motor fuel comprising a major portion of hydrocarbons boiling within the gasoline boiling range, a minor portion of iron tricarbonyl mercaptide but sufficient to raise the anti-knock rating of the motor fuel and lecithin in an amount approximately corresponding to the amount of iron in the mercaptide.

10. A motor fuel in accordance with claim 9 in which the quantity of iron present in the form of iron tricarbonyl mercaptide is between .25 and 10 grams per gallon of motor fuel and the quantity of lecithin ranges from 0.50 to 10 grams per gallon.

11. A motor fuel in accordance with claim 1 in which the metal carbonyl compound is iron pentacarbonyl.

12. The method of preparing a motor fuel of improved octane rating which comprises adding an iron carbonyl compound to said fuel in the presence of a phosphatide in amount at least approximately equal to the amount of iron present as carbonyl compound.

13. The method in accordance with claim 12 in which the iron carbonyl compound is iron tricarbonyl mercaptide.

14. The method of preparing a motor fuel which is sweet to the doctor test and which possesses a high octane number, from a sour motor fuel of low octane number which comprises adding to said motor fuel sufficient polymeric metal carbonyl to react with the mercaptans in said fuel in the presence of sufficient phosphatide to prevent precipitation of metal compounds and

agitating the mixture at a temperature sufficient to cause reaction between said carbonyl and said mercaptans.

15. The method in accordance with claim 14 in which the phosphatide is present in amounts of at least 0.50 gram per gallon.

16. The method in accordance with claim 14 in which the carbonyl is iron tetracarbonyl and the phosphatide is lecithin.

17. The method of preparing a motor fuel which is sweet to the doctor test and which possesses a high octane number comprising adding to sour hydrocarbon motor fuel iron tetracarbonyl

in the presence of sufficient phosphatide to prevent precipitation of iron compounds, said carbonyl being added in amounts sufficient to react with the mercaptans in the motor fuel, heating the mixture to a temperature of approximately 160-180° F. and agitating the mixture at said temperature until the motor fuel is sweet to the doctor test.

18. Method in accordance with claim 17 in which the phosphatide is present in quantities from 0.50 to 10 grams per gallon.

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