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FLUSHING OIL

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The present invention relates to oily liquids adapted for cleaning and lubricating metallic surfaces such as engine parts, and it relates particularly to a composition suitable for use as a flushing oil for removing sludge and other deposits from crankcases of automobile and airplane engines and other types of motors and machinery requiring lubrication at high temperature. This application is a continuation-in-part of application Serial No. 729,234, filed June 6, 1934.

One object of the invention is to provide an oily composition which will have a substantial solvent effect on the sludge or other deposit to be removed and at the same time will have a substantial lubricating value so that any residual flushing fluid will not have any appreciable deleterious effect in the motor or other engine parts when subsequently used. The sludges referred to generally consist mainly of dark colored hydrocarbon oxidation products which are generally emulsified with oil and water due to the formation of metal soaps by combination of organic acids formed by oxidation of the oil with metal parts in contact therewith.

Another object of the invention is to provide a material for flushing and cleaning auto engines which will have not only the above mentioned desirable solvent effect but will also have a suitable boiling range so that it will not be evaporated to any appreciable extent when used for flushing a hot engine and at the same time will not be so high boiling that it would facilitate decomposition when contacted with hot engine surfaces such as the under-parts of the piston head, etc., in an automobile engine.

These and other objects and advantages will be apparent from the following description.

The general procedure used in flushing crankcases of automobile engines, for example, is to drain the used oil out of the crankcase, add flushing oil, run the engine for several minutes, and drain. This procedure must usually be repeated several times if it is desired to have the drainings come out clear. The crankcase is then refilled with clean lubricating oil.

Flushing oils ordinarily used at the present time are light pale oil fractions of petroleum origin, not having sufficient body to be classed as good automotive lubricating oils but having a sufficient body that when a small amount of such oil is left in an automobile crankcase, for example, after the flushing operation is completed, the resulting dilution of the fresh oil which is then added will not cause any harm during the operation of the engine. Such light pale oils generally have a kauri butanol solvent value ranging between 0.5 to 15 or 18 for oils of paraffinic nature and from 15 to 25 for oils of naphthenic nature, and, alone, do not effect a quick enough solvent action on the sludge. This kauri butanol test which is described in Circular 378, Feb. 1931, American Paint and Varnish Manufacturers Association, gives, in comparison to benzol as 100, the amount of liquid being tested which can be mixed with a standard butanol solution of kauri gum without causing turbidity due to insolubility. A more recent article describing in detail the method of making this test and the results obtained thereby as applied to various types of solvents, was published by Baldeschwieler, Troeller and Morgan, in Industrial and Engineering Chemistry, Vol. 7, page 374, November 15, 1935, and was still further amplified in another article by the same authors in the Industrial and Engineering Chemistry, Vol. 9, page 540, November 15, 1937. These articles show that the kauri butanol test is very satisfactory in determining the solvent power of solvents having widely different chemical nature.

As shown in a recent U. S. Patent 2,066,234, the kauri butanol solvent test has also been found satisfactory for determining the gum solvency or gum-fluxing properties of oils used as upper cylinder lubricants in automobile engines and the like.

We have found now, however, that although the materials, which it is preferred to use according to the present invention, all have a fairly high kauri butanol value, i. e. above about 50 and preferably above about 80, still it has been found that the effectiveness of a solvent for use in flushing engine crankcases is not directly proportional to its kauri butanol value. For instance, it has been found that, contrary to expectation, many of the alcohols, ketones and esters such as isopropyl alcohol, acetone and amyl acetate, are of relatively little, if any, value as solvents for use in flushing auto engine crankcases, when used alone, even though these alcohols, ketones and esters all have an infinitely high kauri butanol value, and, on the other hand, it has been found that most of the materials which are preferred, according to the present invention, have kauri butanol values substantially below 200.

Broadly, the present invention comprises preparing a flushing oil with a light pale oil base

stock, preferably having a Saybolt viscosity of about 40 to 300 seconds at 100° F. and incorporating with said base stock a substantial amount, such as at least 5% and preferably 10% or more, of a normally liquid material selected from the group consisting of aromatic hydrocarbons and halogenated hydrocarbons and any relatively cheap commercial products or by-products consisting essentially of such types of materials. Preferably, the solvent to be used should have a boiling point between the approximate limits of 70° and 500° C., preferably between 80° and 200° C., and should have a viscosity between the approximate limits of 30 and 300 seconds Saybolt at 100° F.

Some examples of suitable aromatic hydrocarbons that can be used are benzene, toluene, xylene, and their homologues, and solvent extracts of petroleum fractions rich in aromatic hydrocarbons such as those obtained by extracting light lubricating oil fractions of petroleum with selective solvents such as liquid sulfur dioxide, phenol, nitrobenzene, furfural, etc., or mixtures of various selective solvents, etc. which have a selective solvent action for aromatic (together with some unsaturated aliphatic) hydrocarbons. After the petroleum fraction is treated with such a selective solvent at the desired temperature to effect solution of the desired constituent, the solution is separated from undissolved constituents by gravity or centrifugal separation and the solvent is removed from the solution layer by distillation or other suitable means and thereby an extract is obtained comprising a high proportion of aromatic and unsaturated hydrocarbons. These extracts may be treated, if desired, to remove some of their more unstable constituents. Extracts of this nature have been found to have a relatively high kauri butanol value such as between the approximate limits of 50 and 150, depending upon the boiling range and the origin of the particular stock treated. These extracts may be used directly as flushing oils themselves or may be used as an addition agent to a suitable light hydrocarbon base stock which may be cheaper but less efficient in removing the undesirable sludge from the crankcase. The boiling range of such a solvent extract should be within the approximate limits or 250°–450° C., and preferably within the limits of about 290°–420° C., and may be even narrower, between the limits of 300°–400° C., or even narrower.

Examples of suitable halogenated solvents include carbon tetrachloride, ethylene dichloride, chloroform, ethylene difluoride, chlorinated benzol (referring especially to the mono- and dichlorobenzene) and halogenated oils, etc. If desired, such halogenated materials can be used in admixture with soluble amines or other basic oils or materials to prevent corrosion due to any hydrogen halide liberated, although at least the halogenated aromatic compounds are generally sufficiently stable to not require any such corrosion inhibitor.

Mixtures of these various aromatic and halogenated hydrocarbons may be used and also they may be used along with other solvents such as some of the oxygenated hydrocarbons mentioned previously, namely, alcohols, ketones, esters, and the like.

The viscosity and solvent power may be adjusted at will by blending of solvents, for instance, a viscous high boiling solvent may be thinned out with a very fluid light solvent such as naphtha, isopropyl alcohol, acetone, and the like. The finished compounded flushing oil should preferably have a Saybolt viscosity of about 50 to 150 seconds at 100° F.

One may use two or more flushes: first, thin (low viscosity) and high solvent power; second, higher viscosity but lower solvency. Various combinations such as high viscosity pale oil with low viscosity solvent and vice versa may be used.

The amount of the solvent material to be added to the pale oil base should be at least about 5% of the total flushing oil volume, but will, of course, depend upon the solvent power of the base stock itself and of the solvent to be added as well as the viscosity of the mixture, the temperature at which it is to be used, etc., and within the broader scope of the invention these proportions may be varied at will in order to obtain any particular type of composition having solvent, viscosity, boiling point range and other properties approximately within the desired limits as set forth above. 100% solvent may be used if economically feasible, such as with SO_2 extract of proper viscosity and boiling range, chlorinated petroleum fractions, etc., although with substantially pure compounds, the amount should generally be about 10%, 15%, 20%, 30% or more; however, for special cases, as for cleaning oil filters, etc., one may use 50% or more and even 100% of solvent.

The following table gives the kauri butanol value and boiling point of a few of the materials available for use according to the invention:

	Kauri butanol value	Boiling point
		°C.
Aromatic hydrocarbons:		
SO_2 extract of oil (light lube oil range)	50–150	290–420
Phenol extract of oil (light lube oil range)	50–85	290–420
Benzol	100	80
Toluene	93.8	110
O-xylene	99	138
Chlorinated hydrocarbons:		
Aromatic—		
Mono-chlorobenzene	110	132
Di-chlorobenzene	117	173–179
Aliphatic—		
Chloroform	157	61
Carbon tetrachloride	91	77
Ethylene dichloride	82	84

The following specific examples are suggested as illustrative of the invention:

Example 1

33% of sulfur dioxide extract of petroleum obtained when treating kerosene for improvement in burning quality (having a boiling point range from about 150 to 250° C. and having a kauri butanol solvent value of about 65) was incorporated with a light pale oil of naphthenic origin having a viscosity of about 200 seconds Saybolt at 100° F. This composition was found to have a kauri butanol value of about 45 and was found very suitable for loosening and removing deposits of sludge in automobile crankcases.

Example 2

An automobile engine oil filter plugged up with sludge deposits was disconnected from the oil lines leading to the engine and was washed by passing dichlorethane through it first until the sludge was removed and then with naphtha to remove the residual halogenated solvent and then reinstalled in service. If desired, it could have been given a final wash with light pale oil to remove residual naphtha.

EXAMPLE 3

A mixed solvent consisting of 60% benzol, 30% alcohol and 10% acetone was blended with 70% hydrocarbon flushing oil; the mixture had a Saybolt viscosity of 100 seconds at 100° F.

Although it is obviously difficult to make actual engine flushing tests which are comparable in all respects due to the fact that different engines have different operating characteristics and if the same engine is used, other factors become of importance such as weather conditions, time, etc., nevertheless the following actual engine flushing tests are reported in order to show that the invention has actual practical value.

TEST 1

An automobile engine of a well-known common make having 8 cylinders in all, 4 on each side set in the form of a V, with a mileage of 9,304 recorded, was first inspected. In the pan, heavy sludge was found in the corners and on the bottom after the lubricating oil had been allowed to drain off, the drain hole being set too high in the pan to completely empty the crankcase. In the upper part of the crankcase, sludge was found in the corners and on the pump shaft, slight sludge being present on the screen. 3 quarts of a commonly used flushing oil which was a treated paraffin oil having an A. P. I. gravity of at least 28°, flash of 335° F., A. S. T. M., and a Saybolt viscosity of 108 to 113 seconds at 100° F., were added and the automobile was driven for 65 miles of normal driving. After the flushing oil was allowed to drain off, it was found that considerable sludge had been removed from the corners and a thin sludge was found on the bottom due to the height of the drain hole in the crankcase. The upper section of the crankcase was slightly improved and the effectiveness of the flushing oil was estimated as 20%.

TEST 2

Another automobile of a different make and having a 6-cylinder motor with a mileage on the odometer of 14,645 was inspected and it was found that after draining the flushing oil, light sludge was present in the corners. There was hard sediment and road dirt on the bottom of the crankcase. In the upper part of the crankcase was found heavy, solid-like sludge in the left corner, medium sludge in other corners, on oil lines and on crank throws. The oil screen was two-thirds plugged. To this crankcase were then added 4 quarts of the same flushing oil used before, having a gravity of about 20° A. P. I., together with 25% of isopropyl alcohol. The engine was allowed to idle at a fast rate of speed for 20 minutes, after which the flushing oil was drained. On inspection, the pan disclosed a slight amount of sludge which had been removed. From the upper part of the crankcase a slight amount of sludge was also found removed. The binder appeared partially dissolved and the oil screen was not clean. The effectiveness was considered about 10%.

TEST 3

Another car of the same make and number of cylinders as the one used in Test 1, and having an odometer reading of 5,971, was used for this test. After the oil that had been used was removed, the pan was found to contain medium to heavy sludge in the corners, ends and on the bottom. The drain hole was also too high to remove all the liquid from the crankcase. In the upper part of the crankcase, sludge was found in the corners and on the pump shaft and engine parts. Into this crankcase were added 5 qts. of a mixture consisting of ⅔ by volume of Coastal pale oil having a Saybolt viscosity of 500 seconds at 100° F. and ⅓ by volume of an extract prepared by extracting a light lubricating oil with sulfur dioxide and then washing the extract with soda. The mixture had a Saybolt viscosity of 82.4 seconds at 100° F. and 36.9 seconds at 210° F. After being driven 77 miles, the crankcase was drained and it was found that considerable sludge had been removed from the corners. A thin sludge was found present on the bottom. Considerable sludge was removed from all engine parts. The effectiveness was considered as 25%.

TEST 4

Another standard 6-cylinder car having an odometer showing 39,305 miles was used for the next test. Upon draining the lubricating oil from the crankcase of this automobile, light, soft sludge was found on the ends and hard sludge on one spot on the bottom. In the upper part of the crankcase, light and medium sludge was found present in the corners, traces of sludge on throws and the screen was two-thirds plugged with a mayonnaise-type of sludge. The valve chamber contained medium to heavy sludge. To this crankcase was then added 3 quarts of common flushing oil of about 28° A. P. I. gravity, together with 14% of dichlorobenzene. The engine was allowed to idle at a high rate of speed for 20 minutes. Upon draining the flushing oil, the pan, on inspection, disclosed that the sludge had been mostly removed from the ends and that the sludge on the bottom was slightly attacked. From the upper part of the crankcase a slight amount of sludge had been removed. The screen was materially improved, although the oil lines were partially cleaned. The valve chamber did not show any improvement. The effectiveness was about 30%.

The above 4 tests are summarized in the following table:

TABLE 1

Crankcase flushing tests

Test No.	Flushing liquid	Estimated per cent effectiveness	Per cent improvement compared to common flushing oil
1	Common flushing oil	20	
2	"1" containing 25% isopropyl alcohol.	10	−50
3	"1" containing 33% SO_2 extract.	25	+25
4	"1" containing 14% dichlorobenzene.	30	+50

It is obvious, of course, that the invention can be made still more effective if mechanical means are used to aid the flushing, for instance, by agitation as by air blowing, etc., or by injecting the flushing liquid into the crankcase in the form of a spray under pressure in one or more fine jets.

It is apparent from the above table and description of the crankcase flushing tests that the use of 33% of sulfur dioxide extract (which is rich in aromatic hydrocarbons) accomplished a very considerable (25%) improvement in the effectiveness of the common flushing oil and the use of 14% of dichlorobenzene effected a 50% improvement in the effectiveness of the common flushing oil. These are very remarkable results because, as stated in the beginning, the sludges

which accumulate in engine crankcase are extremely difficult to remove due to the fact that they consist of complex emulsions containing, in addition to oil itself, water, metal soaps and various hydrocarbon oxidation products derived from oxidation of the lubricating oil. The presence of the water is particularly troublesome, and makes the problem vastly different from that of removing carbonaceous and gummy deposits from the combustion chamber of an engine, because most of the best solvents for the organic constituents of the sludge are insoluble in water and therefore the water particles in the sludge emulsion tend to resist attack by the organic solvents.

In order to still further emphasize the difference between the removal of sludge from engine crankcases as compared to the removal of carbonaceous and gummy deposits from the engine combustion chamber, it should be noted that a large number of compositions recommended in the literature and patents as particularly suitable for removing carbonaceous and gummy deposits from the combustion chamber were tested for their effectiveness for that purpose and the vast majority thereof proved to be of little, if any, value and really only one was actually what was considered very effective and that one was an onium base such as tetramethyl ammonium hydroxide as recommended in Patent 2,047,191. On the other hand, that material, the only really effective one for removing carbonaceous and gummy deposits from the combustion chamber of an engine, is totally unsuitable for use in flushing oils for several reasons, chief of which are that such a material, being a strong alkali, would immediately saponify the organic acids present in the crankcase sludge and, since the soaps are good emulsifying agents, such an onium base would therefore immediately aggravate the emulsion troubles in crankcase sludges, and furthermore would be definitely unsatisfactory because it would attack some of the metals and alloys present in the bearings in the engine. Therefore, it is clear that not only are the problems vastly different between removal of crankcase sludges as compared to removing carbonaceous and gummy deposits from the combustion chamber but also the solution of these problems must apparently also be different and consequently the greatly improved results obtained by the present invention are highly unexpected.

The advantages of the invention may be still further seen from the following description of some laboratory tests on the relative effectiveness of various flushing oil compositions in dispersing two sludges:

One sludge was a stiff water-resistant sludge obtained from the filter on the Hercules engine. This sludge was taken from the engine after it had run 84 hrs. at 1500 R. P. M. and 45 brake horse power on Coastal oil, S. A. E. 30, vis. 55 sec. Saybolt at 210° F. The other sludge was a synthetic sludge composed of 15% carbon black, 15% water, 2% acid-free Al-Ca soap of #6 cut acids obtained in sweater oil oxidation, and the remaining 68% was a high quality S. A. E. 40 lubricating oil available on the market, which had been oxidized at 300° F. for 336 hrs. with 10 liters of air per hour. This sludge was homogenized by passage through a colloid mill.

To 5 grams of the Hercules sludge in a test tube 60 ccs. of the experimental flushing oil were added, and the tube was agitated by shaking vigorously. In the case of the synthetic sludge, 15 ccs. were used and similarly shaken with the experimental flushing compositions.

Observations were made during agitation of the ease with which the sludge could be dispersed. The results obtained are summarized in the following Table 2. Here the oils are rated in three classes. The oils that dispersed the sludge within 30 seconds but did not hold it in suspension for an equally long period and did not completely absorb the water are rated as "A." Class "B" refers to oils which dispersed sludge less quickly (30 to 60 seconds), gave poorer suspension than Class "A" and did not absorb the water at all. In Class "C" are placed compositions which dispersed the sludge only after one to four minutes of agitation. It is considered that only those flushing liquids are satisfactory which have an "A" or "B" rating as to both the synthetic sludge and the Hercules sludge.

TABLE 2

Classification of experimental flushing oils in the order of their effectiveness in dispersing two sludges

	Agent*	Synthetic sludge	Hercules sludge	Kauri butanol value
1	Di-chlorobenzene	A	A	
2	Toluene	A	A	93.7
3	Chlorobenzene	A	A	
4	Chloroform	B	B	157
5	Ethylene dichloride	B	B	82
6	Benzene	B	B	1.0
7	"Solvent oil" (aromatic extract of a naphthenic oil)	B	B	50–150
8	Amyl acetate	B	C	
9	Dibutyl phthalate	B	C	
10	Hexyl alcohol	C	B	
11	Cyclohexane	C	C	
12	Secondary amyl alcohol	C	B	
13	Isopropyl alcohol	C	C	
14	Common flushing oil	D	D	30

*All but #7 (which was run undiluted) were tested in 20% concentration in the common flushing oil.

The common flushing oil, with no added solvent, failed to take up the entire sludge completely even on prolonged shaking and so was unsatisfactory. Both the compositions containing the chlorinated compounds and those containing aromatic solvents materially improved the sludge-dispersing properties of the common flushing oil. The oxygen-containing compounds such as esters and alcohols, and naphthenic hydrocarbons such as cyclohexane proved definitely unsatisfactory because they were poor in at least one of the tests which is interpreted to mean that although they might be satisfactory some of the time in commercial use, yet at other times they would be unsatisfactory and therefore unreliable. A flushing oil should be able to remove sludges obtained from all types of lubricating oils in all types of engines and resulting from a wide variety of conditions of engine operation and climatic changes.

In the appended claims the term "flushing oil" is intended to mean an oily liquid adapted to remove sludge and other deposits therefrom and otherwise clean and lubricate the crankcases of internal combustion engines and other metallic surfaces of machinery normally in contact with lubricating oil at high temperature during use.

In using extracts prepared by treating petroleum fractions with solvents having preferential solvency for aromatic and unsaturated hydrocarbons, either the whole extract may be used or various fractions of it such as, for example, the

40% lightest fractions of the extract described in Example 1.

It is not intended that the invention be limited to any of the specific examples hereinabove given nor to any theories advanced as to the operation of the invention, but in the appended claims it is desired to claim all novelty in the invention as broadly as the prior art permits.

We claim:

1. A flushing oil for cleaning internal combustion engine crankcases having a kauri butanol solvent value between about 40 and 200 and to which has been added at least about 10% of at least one normally liquid material selected from the group consisting of aromatic hydrocarbons and halogenated hydrocarbons.

2. A flushing oil for cleaning internal combustion engine crankcases consisting essentially of a base stock of a petroleum fraction having the usual flushing oil boiling and viscosity characteristics and having a kauri butanol solvent value not greater than 30, having added thereto at least about 10% of a normally liquid material selected from the group consisting of aromatic hydrocarbons and halogenated hydrocarbons sufficient to raise the kauri butanol solvent value of the mixed composition to at least about 40.

3. A flushing oil for cleaning internal combustion engine crankcases consisting essentially of a petroleum hydrocarbon base stock having a viscosity between the approximate limits of 30 and 300 seconds at 100° F. and a boiling range between the approximate limits of 100° C. and 500° C., containing about 15–50% of mono- or di-chlorobenzene.

4. The method of cleaning internal combustion engine crank cases which comprises flushing them at least once with a liquid composition having a kauri butanol solvent value not lower than about 40 and containing at least about 10% of a normally liquid material selected from the group consisting of aromatic hydrocarbons and halogenated hydrocarbons.

5. The method of cleaning internal combustion engine crank cases which comprises flushing them at least once with a liquid composition which consists essentially of a petroleum hydrocarbon base stock having a viscosity between the approximate limits of 30 and 300 seconds at 100° F., a boiling point range between the approximate limits of 100° C. and 300° C. and a kauri butanol solvent value not substantially above 30, said flushing oil also containing at least 10% of a normally liquid material having a kauri butanol solvent value between the approximate limits of 50 and 200 and selected from the group consisting of aromatic hydrocarbons and halogenated hydrocarbons.

6. Method according to claim 5 in which the flushing liquid contains about 15–50% of mono- or di-chlorobenzene.

7. The method of cleaning internal combustion engine crank cases which comprises flushing them at least once with a flushing oil containing at least 20% of a petroleum fraction rich in aromatic hydrocarbons, which fraction has been obtained by treating a crude petroleum fraction having a boiling range not substantially lower than that of kerosene and not substantially higher than that of pale lubricating oil, with a selective solvent such as liquid sulfur dioxide, phenol and the like having a selective solvent action for aromatic hydrocarbons.

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