

[54] **METHOD OF PURIFYING LUBRICATING OILS**

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[57] ABSTRACT

A method of purifying used lubricating oils comprising the following steps:

1. Admixing the used lubricating oil with a mutually soluble predominantly hydrocarbon liquid diluent which preferably has a boiling range within the temperature region of about 100°F. to about 550°F.;
2. Admixing the diluted lubricating oil with a water miscible alcohol and water mixture containing a small amount of an ammonium or alkali metal base, and
3. Centrifuging to remove sludge and metal compounds from the oil and to separate the diluted oil phase from the alcohol-water phase to provide a purified organic layer having a low ash content.

20 Claims, No Drawings

METHOD OF PURIFYING LUBRICATING OILS

The United States and other industrialized countries are faced with an increasing scarcity and increased cost of petroleum and petroleum products. Paradoxically, the industrial nations of the world are also faced with tremendous problems in utilizing used petroleum products without contaminating the environment.

High viscosity index lubricants, as employed for automobile lubrication, present a tremendous problem to the environment. Such lubricants commonly contain relatively large amounts of various detergents and extreme pressure additives in the form of polyvalent metal soaps as well as lead compounds, oxidized carbonaceous materials, water, etc. Due to their relatively high content of various additives, used lubricating oils cannot be burned simply without seriously polluting the air. Thus, literally millions of gallons of used lubricants are discarded annually because there is no economical way to recycle them.

Various methods have been employed to clean waste lubricating oils so that they may be reused. In general, these methods currently have been unsuccessful due primarily to economic factors.

Due to the change in the composition of lubricating oils through addition of additives such as soaps, E.P. agents, VI improvers and polymeric dispersants, the quantity of lubricating oil which can be recovered economically by reclaiming procedures has decreased. Thus, at present, the yield of lubricating oil which can be obtained by reclaiming is in the order of 50 percent or less of the recoverable organic material. Due to the severity of treatment, a substantial quantity of the recoverable organic material in the oil is lost. This makes the reclaiming procedure less economical and also results in the production of an increased quantity of sludge and byproducts whose disposal causes contamination of the environment.

In one method of treatment which has been used, the used lubricating oil is first treated with caustic at an elevated temperature such as 400° to 600°F. to drive off water and to break soaps in the oil as well as to neutralize the oil. Also, in the course of heating, the light ends are flashed off and are generally burned. After the heating procedure, the oil is then cooled to about 100°F. or less and a small quantity of concentrated sulfuric acid is added. After settling, the bottoms are drawn off which contain an acid sludge comprising sulfuric acid and dissolved sulfonates and oxygenated hydrocarbons. The sludge, which may constitute about 5 to 20 percent by weight of the used oil being treated, is disposed of by being placed in a closed container to prevent the escape of acid fumes. The sludge is then dumped. Due to the noxious properties of acid sludge, it is presently very difficult to find a landfill which will accept material of this type. For example, in the Los Angeles area, acid sludge is hauled to San Diego where there is a landfill having a high lime content which will accept acid sludge.

After removal of the acid sludge from the oil, the top oil is then generally heated and finely divided clay is added at a temperature of about 350°F. The mixture of clay and top oil is then taken to a temperature of about 600°F. in a heater and after being held at this temperature for sufficient time is cooled to about 350°F. or less and passed through a filter press.

The above procedure, which is one of the procedures used for reclaiming lubricating oil, gives, at best, a yield of only about 50 percent reclaimed oil based on the weight of the used oil which was treated. The procedure produces large quantities of acid sludge which is difficult to dispose of. Also, the process requires substantial heating, which is expensive, as well as the use of expensive chemicals which are not recoverable.

Another procedure which has been used for treatment of used lubricating oils involves treatment of the oil with lime and finely divided clay. A still further procedure involves treatment of the oil with a mixture of caustic and sodium silicate. All of the above noted procedures give a yield of purified oil of 50 percent or less based on the weight of the used oil being treated together with the production of 5 to 20 percent of light ends or tops which are burned. Additionally, all of the above procedures produce substantial quantities of sludge which cannot be recycled and must be dumped.

In providing a solution to the aforementioned problems, the present process for the purification of used lubricating oils is economical — providing a yield of about 80 percent to about 95 percent or more of the recoverable organic material in the used oil — and also produces a very small amount of residue composed of polyvalent metal compounds in admixture with oxidized hydrocarbons and all of the myriad materials which are found in the sludge from used lubricating oils. Thus, the process provides a means for substantially reducing environmental pollution resulting from the dumping of waste oil. Also, the process provides a new source of high viscosity index oils which are presently in short supply and are urgently needed in industrialized countries for automotive lubrication.

In accord with the process, used lubricating oils, which may be collected from various sources, such as independent service stations throughout a large area, are first admixed with a predominantly hydrocarbon liquid diluent which preferably has a boiling range within the temperature region of about 100°F. to about 550°F. The liquid diluent may be either aromatic or aliphatic and is mutually soluble with the used hydrocarbon lubricating oil undergoing treatment. The function of the liquid diluent in the process, as envisioned, is to lower the viscosity of the used lubricating oil and to change the characteristics of the used lubricating oil dispersion to thereby facilitate the contact, with the used lubricating oil in the subsequent steps of the process, of a water miscible alcohol-water mixture.

The term "predominantly," as used in defining the hydrocarbon content of the liquid diluent, refers to a liquid whose hydrocarbon content is about 90 percent by weight or greater. Impurities which may be present in the liquid diluent, which may be recycled light ends from the purified lubricating oil, may include, for example, small quantities of sulfur-containing compounds, such as mercaptans, and oxygenated hydrocarbons such as aldehydes or ketones. The impurities which may be present in the liquid diluent will vary depending on the makeup of the used lubricating oil which is the source of the recycled light ends. Thus, the above listing of impurities is not intended to be all inclusive.

Preferably, the predominantly hydrocarbon liquid diluent has a boiling range within the temperature region of about 100°F. to about 500°F. although lower

boiling hydrocarbon liquids, such as liquid propane, may also be employed. The purified lubricating oil produced in accord with the process may be subjected to distillation. In the course of the distillation, the light or naphtha ends may be recycled to the process to serve as the predominantly hydrocarbon liquid diluent for the used lubricating oils being treated. Thus, after initial start-up, the process will be self-sustaining with sufficient naphtha light ends being supplied through distillation of the purified oil or organic phase to satisfy the need for liquid diluent in diluting the as received used lubricating oil.

The quantity of the liquid diluent which is employed in diluting the as received used lubricating oil may be varied in accord with the process. A particularly practical range of liquid diluent with respect to used oil ranges from about 1:1 to about 1:2 by volume, although other dilutions may be used, if desired, such as 2:1 or even 4:1 depending, for example, on the solids content and viscosity of the used drain oil undergoing treatment and the efficacy of the diluent liquid in furthering contact by the extraction solvent.

Generally, it is desirable to use the smallest amount of diluent possible since an increase in the amount of diluent makes the subsequent separation of the diluent and the oil more involved and costly. For example, when the amount of diluent is increased, the size of the separation equipment, such as distillation columns, etc., must also be proportionately increased which causes an increase in the cost of the processing equipment.

After dilution of the used lubricating oil undergoing treatment with a predominantly hydrocarbon liquid diluent, as described, the diluted lubricating oil is then contacted with a mixture of water, a water miscible alcohol, and a small quantity of an ammonium or alkali metal base. Although not bound by any theory, it is believed that the ammonium or alkali metal base, which includes ionizable salts that form the base in situ, functions to displace polyvalent metal ions from the various metallic soaps which are present in the diluted lubricating oil undergoing treatment. As the polyvalent metal ions are displaced from the soaps by the monovalent ammonium or alkali metal cations, the molecular weight of the soaps is decreased. With the decrease in molecular weight of the soaps, their solubility in the diluted lubricating oil is also decreased while their solubility in the water-alcohol phase is increased. This phenomena is believed to facilitate the extraction of the metal soaps from the diluted lubricating oil through contact with the water miscible alcohol-water mixture. Also, for reasons which are not understood, the resultant change in the dispersant composition of the oil phase releases the peptized solids which may then be removed by centrifugation as will be described.

Among the water miscible alcohols which may be used in this step of the process are methanol, ethanol, isopropyl alcohol, *n*-propyl alcohol, sec-butyl alcohol, and tert.-butyl alcohol. The higher alcohols, such as amyl alcohol and also alcohols having a lower water solubility such as *n*-butyl alcohol, have such a low solubility in water that they are generally ineffective in the present process. Thus, the water miscible alcohols which are suitable in the process, including polyhydric alcohols, generally have a solubility of about 20 percent or more by volume in water.

Of the various alcohols, it was found that isopropyl, *n*-propyl and tert.-butyl alcohol functioned best in the performance of the process. Moreover, it was found that alcohol-water mixtures containing from about 40 percent to about 60 percent by volume of alcohol were generally more effective than mixtures containing either more or less alcohol in relation to the amount of water in the alcohol-water mixture.

In describing the present process, it should be emphasized that the material undergoing treatment, i.e., used lubricating oil, is not a homogeneous material. Thus, in practice, the specific operating conditions employed may be varied to suit the particular batch of lubricating oil which is being treated. For example, if the batch of lubricating oil undergoing treatment has a relatively high water content, this factor may be taken into consideration in determining the ratio of alcohol to water in treating the lubricating oil after it has been diluted with a predominantly hydrocarbon liquid diluent as described.

In determining the optimum process conditions for a particular batch of used lubricating oils, the lubricating oils may, for example, be collected in a relatively large holding tank. When the holding tank is full, representative samples may then be taken and analyzed with a view to determining the optimum process conditions for treating the used oil in that tank. By way of example, the behavior of the samples may be determined by considering how much of the predominantly hydrocarbon liquid diluent available for processing to mix with the used lubricating oil, on a volume-to-volume relationship to obtain the optimum basis for handling and centrifugation. Also, to determine optimum conditions, samples of the used lubricating oil in the holding tank may be treated on a small scale according to the present process to determine the conditions which provide the greatest reduction in the ash content of the oil being treated and the greatest yield of purified oil.

A particularly suitable quantity of the water miscible alcohol-water mixture is about one volume of the mixture for each volume of the diluted used lubricating oil for one-stage extraction of the diluted lubricating oil. The diluted lubricating oil may be subjected to multiple-stage extraction with a water miscible alcohol-water mixture, as described, and also the quantity of the alcohol-water mixture may be varied, for example, from about one-half volume of alcohol-water mixture to two volumes of the diluted lubricating oil to higher volume ratios in excess of 1:1. In general, the volume of the water miscible alcohol-water mixture is kept as low as possible since this simplifies the subsequent processing steps in terms of equipment size, cost, etc.

Various water soluble ammonium and alkali metal bases may be employed in the alcohol-water mixture used in treating the diluted lubricating oil. To illustrate, ammonium carbonate, sodium carbonate, potassium carbonate, lithium carbonate, and sodium hydroxide have all been employed and found suitable. Of the various bases which have been employed, sodium carbonate and sodium phosphate are preferred. Although not bound by any theory, it is believed that the carbonate and phosphate anions are particularly effective in reducing the solubility of the polyvalent metal cations which are displaced from the metallic soaps in the diluted lubricating oil by the nonvalent ammonium and alkali metal ions, and in reducing the efficacy of the non-ionic dispersants remaining in the oil to maintain

the micellar configuration necessary to keep the solids and sludge in dispersed form in the diluted oil. Surprisingly, closely related anions, such as the bicarbonate ion, were found to be less effective in the process than the carbonate ion.

It has been found that the use of excessive quantities of the water soluble ammonium or alkali metal base actually causes a reduction in the overall efficiency of the process, i.e., by producing a purified oil whose ash content is higher than that which is obtained through use of a smaller quantity of the base. Although not bound by any theory, it is believed that this result occurs because of the presence of non-ionic detergents which are also present in used lubricating oils. When excessive quantities of the monovalent cation base are employed, which are in excess of that required to displace the polyvalent metal cations from soaps within the oil, the additional sodium is believed to be taken up by the non-ionic detergents. This would increase the ability of the non-ionic detergents to suspend sludge and metal within the oil. As a result, the purified oil obtained from the process will have a higher ash content than that obtained by using a lesser quantity of the ammonium or alkali metal base.

For the above reasons, it is preferred that the quantity of the ammonium or alkali metal base which is used is sufficient to displace the polyvalent metal ions from the soaps within the oil but that the base not be present in any great excess of that amount. As an example, in treating a diluted used lubricating oil (containing one-half volume of used lubricating oil admixed with one-half volume of a liquid predominantly hydrocarbon diluent) by mixing with one volume of a 50:50 volume ratio water miscible alcohol-water mixture, it was found that the use of one gram of an alkali metal base, e.g., sodium carbonate, for each 100 mls. of the alcohol-water mixture gave satisfactory results.

Agitation is generally employed during the treatment of the diluted lubricating oil with the alcohol-water mixture containing an ammonium or alkali metal base. For example, the agitation may be provided by mixing within a large vessel through use of a mixing impeller, in a continuous, metered in-line mixing device such as a gear pump or homogenizer, or by using any other mixing procedure.

The agitation of the diluted lubricating oil and alcohol-water mixture is generally carried out until an emulsion forms which indicates that the diluted oil has been thoroughly contacted with the alcohol-water mixture. The emulsion is generally unstable and is broken during the subsequent centrifuging step. If the emulsion is not broken during centrifuging, this is undesirable since the process yield is reduced by trapping of recoverable oil in the emulsion phase. It is preferred that the formation of a stable emulsion which is not broken by centrifuging be kept to a minimum. This may be accomplished by taking representative samples of the used oil being treated and then varying the process parameters on a small scale to determine the optimum yield conditions. By determining the optimum processing conditions for a particular used oil, the formation of a stable emulsion may be minimized to provide the maximum yield of recoverable organic material in the oil.

Following the treatment of the diluted lubricating oil with the alcohol-water mixture, as described, the resulting mixture is then fed to a centrifuge for separation

of the sludge from the lubricating oil and also separation of the alcohol-water mixture from the organic mixture of liquid diluent and lubricating oil. Industrial centrifuges are well known and any of the various types of centrifuges may be used in the present process. The resultant mixture is simply fed into the centrifuge with the sludge depositing out on the walls of the centrifuge while the alcohol-water mixture is taken off through one outlet and the organic mixture of liquid diluent and lubricating oil is removed through another outlet. Periodically, the sludge formed on the interior of the centrifuge may be removed by back-washing or by spraying the interior of the centrifuge bowl with a jet of water. These various procedures for removing solids from industrial centrifuges are well known.

The alcohol-water stream which is taken from the centrifuge contains ammonium or alkali metal soaps. Depending upon the soap content of the alcohol-water mixture, the mixture of water miscible alcohol and water may be recycled directly to the process for use in treatment of used lubricating oil diluted with a predominantly hydrocarbon liquid, as described. However, the alcohol-water stream may also first be subjected to a clean-up operation before return to the process. Any conventional procedure may be used for cleaning the alcohol-water stream to remove alkali metal soaps such as acidification and extraction of the organic acids, ion exchange, or distillation of the alcohol followed by addition of fresh make up water to the alcohol, etc.

The mixture of purified lubricating oil and predominantly hydrocarbon liquid diluent may be used as a low ash fuel or the mixture may be separated through conventional distillation. The naphtha fraction from the distillation may, as described previously, be recycled for use in the process in diluting the used lubricating oil. The purified lubricating oil fraction from the distillation may be used as the base stock in compounding new lubricating oils.

A convenient and accurate way of measuring the effectiveness of the present process in terms of the purity of the lubricating oil obtained is to compare the ash content of the as is used lubricating oil with the ash content of the purified lubricating oil product obtained from the process. Based on experiments carried out with four used lubricating oils obtained from various sources, the present process may provide a reduction in the ash content of the oil of 80 to 90 percent. For example, an ash content of about 2 percent in the as received used oil was reduced to about 0.2 percent in the purified oil. In addition, of course, there is a reduction in the additive content of the oil which simplifies further processing of the purified oil using conventional refinery procedures.

The residue from the process, which consists of the various materials that are present in the sludge of a used lubricating oil may constitute about 3 percent by weight of the as received used lubricating oil. Thus, the residue is only a very small fraction of the weight of the used lubricating oil. By greatly reducing the weight of the residue removed from the used lubricating oil during purification, the process does not present the problems of waste disposal which have plagued previous attempts to process used lubricating oils.

The residue from the process has a high metallic content, predominantly lead, and, thus, represents a potentially valuable source of metals. In view of the large

quantity of used lubricating oil which is generated by crankcase drainings from automobiles, the process residue from all the used oil would be quite sizable in terms of total weight of metals, even though the residue represents only a small percentage by weight of the used lubricating oil being treated. Thus, the residue may be processed, where economically feasible, to recover its metal fractions.

The examples described in the following tables were generally conducted by mixing a measured volume of a used drain oil with a measured volume of an indicated predominantly hydrocarbon liquid diluent. After mixing the drain oil and diluent, the diluted oil was then admixed with a specified alcohol-water mixture, thoroughly agitated, and then centrifuged for four hours.

The method of centrifuging used was a modification of ASTM method D1796-62. In centrifuging, 100 ml. cone shaped tubes (described in the ASTM method) were first filled with the resultant mixture formed from the diluted drain oil and the mixture of alcohol with water. The cone shaped tubes and their contents were then whirled in a Precision Oil Centrifuge (Catalog No. 67343) to produce a relative centrifugal force of 800 at the tips of the tubes.

On completion of the centrifuging, the contents of the tubes had separated into several layers. At the bottom of the tube was a layer of sludge which had been removed from the drain oil by the process of the invention. Above the lower sludge layer was a water miscible alcohol-water layer and above this layer was an organic layer containing a purified organic phase of the predominantly hydrocarbon liquid diluent with the purified drain oil. This upper layer is termed the organic layer. In some of the examples, an emulsion or dispersion formed which was not completely broken by the centrifuging and which appeared within the organic or the alcohol-water phase or as a layer at the interface between the organic layer and the alcohol-water layer.

The yield of recoverable organic material in volume percent of the drain oil was determined by measuring the volume of the purified organic layer and subtracting the volume of the hydrocarbon liquid diluent from this volume. The remaining volume, which is the volume of the recovered organic material from the drain oil, was then divided by the original volume of the drain oil to determine the percent yield of recoverable organic material. In some instances, as indicated in the tables, the yield of recoverable organic material from the drain oil was observed to be in excess of 100 percent. In these instances, a dispersion or emulsion was observed and there had obviously been a transfer of material into the organic layer which produced the high reading.

After centrifuging, as described above, a sample was removed from the organic phase using a 100 ml. syringe fitted with a 8 inch needle. The sample from the organic phase was then analyzed to determine its solids content and the ash content of the solids. The ash content of the purified drain oil was then converted to an ash content based on the weight of the original drain oil by multiplying the ash content of the solids by the percent solids in the original oil. This, then, permitted a direct evaluation of the process in terms of the percentage reduction which was obtained in the ash content.

In determining the percentage of solids in the drain oil or the purified organic layer, a 10 gram sample was weighed into a soft, crimped aluminum dish having a diameter of $2\frac{3}{8}$ inches, a depth of $\frac{5}{8}$ inches and a finger-grip handle. The dish was placed on a Corning Pyroceram 600-watt hotplate with a temperature dial set to produce a surface temperature of approximately 450°F. and preheated to the operating temperature. Heating at about 450°F. was maintained for 1 hour, after which the dish was removed, cooled to ambient temperature, and reweighed. The percent of solids was then determined by dividing the final weight of the residue by the weight of the sample and multiplying by 100.

The ash content of the drain oil or the purified organic layer was determined by ASTM method D482-63. In determining ash, the analytical problems which are associated with the presence of phosphorus and lead compounds were disregarded since the results were used on a comparative basis. In other words, any error produced by the presence of phosphorus or lead would have a similar effect in the ash analysis of the used drain oil as in the ash determination for the purified organic liquid. Thus, the errors, if any, would not affect the validity of the comparison of the ash content of the used drain oil with that of the purified organic liquid.

The method for determining ash consists of weighing a sample of the material to be ashed into a 30 ml. porcelain crucible. The material in the crucible is then ignited and allowed to burn until only ash and carbon remain. The carbonaceous residue is then reduced to an ash by heating in a muffle furnace at 775°C., followed by cooling and weighing. As determined by this method, the ash content primarily indicates the metals content of the sample expressed in terms of the inorganic salts of the metals which are predominantly phosphates, oxides, silicates, sulfates, etc.

In determining the ash content of the purified drain oil corrected to the weight of the used drain oil, the solids content and the ash content of the used drain oil were determined as a percentage of the weight of the drain oil sample. The ash content of the purified organic layer was also determined as a percentage based on the solids content of the sample from the purified organic layer. Conveniently, the weight of solids of the purified organic layer was determined and these solids were then burned to determine the ash content of the solids. The ash content of the purified organic layer, expressed as a percent of the solids in the sample, is then converted to weight percent ash based on the used drain oil by multiplying by the percent of solids in the used oil.

The basis for the conversion of the ash in the purified organic layer to percent ash based on the used drain oil is based on the fact that the ash is contained in the solids and the total solids content of both the drain oil and the purified organic layer is relatively constant and is only slightly affected by the present process. In the course of heating at about 450°F. to determine solids, the liquid hydrocarbon diluent in the sample from the purified organic layer is driven off. Thus, the solids which remain are those obtained from the used drain oil being treated. Likewise, in determining solids in the used drain oil, the heating at about 450°F. drives off the light fractions as well as any water present in the drain oil. The solids which remain are largely hydrocarbons

which have a boiling point in excess of 450°F., and these solids are almost entirely recovered by the present process.

The solids content changes slightly as a result of the present process since the sludge and metals which are removed from the used drain oil are solids. However, the weight of the solids which are removed is very small in comparison to the total weight of solids composed mainly of hydrocarbons whose boiling point is in excess of 450°F. For these reasons, the assumption that the solids content from the drain oil remains fixed throughout the process is reasonably valid and any errors resulting from this approximation are within an error of about 5 percent of the observed values, i.e., ± 0.05 times the observed values.

TABLE I

Example No.	Drain Oil of 1.44% (wt.) Ash		
	1	2	3
Drain Oil (mls.)	25	25	50
Naphtha Diluent (mls.)	25	25	50
50% (vol.) Isopropyl Alcohol-Water (mls.)	50	50	
Na ₂ CO ₃ (gm/100ml Alc-Water)		2	
Recovery of Drain Oil-Vol.%	102	98	98
Ash of Recovered Drain Oil-Wt.%	0.84	0.28	0.92
Dispersion-Organic Layer	None	None	Yes
Dispersion-Alcohol Layer	Yes	None	

As shown in Table I, Examples 1-3 are each concerned with a drain oil having an ash content of 1.44 percent by weight. In Example 1, the ash content was reduced to 0.84 percent, based on the weight of original drain oil, while in Example 2 the ash content was reduced to 0.28 percent. The striking effect of adding a base to the alcohol-water mixture is illustrated by the results of Example 2 in which all of the process conditions were otherwise the same as in Example 1. Example 3 illustrates the effect of dilution in which 50 mls. of drain oil were admixed with 50 mls. of naphtha diluent and then centrifuged directly without being contacted by the alcohol-water mixture. As shown, there was some reduction in the ash content obtained by dilution of the drain oil with a hydrocarbon diluent and centrifuging. However, this reduction in ash was far less than that obtained, for example, in Example 2 where

the diluted drain oil was thoroughly admixed with 50 mls. of a 50 percent by volume mixture of isopropyl alcohol and water which contained a small quantity of a base.

In Examples 4(a), 4(b), 5 and 6 shown in Table II, the used drain oil undergoing treatment had an ash content of 1.65 percent by weight. In Example 4(a), the ash content was reduced to 0.20 percent by weight, based on the weight of the original drain oil, in one stage. In a second stage, shown as Example 4(b), 50 mls. of the purified organic phase from Example 4(a) were admixed with 50 mls. of an alcohol-water mixture containing 1 gram of a base and subjected to further centrifugation. As shown, the second stage of the procedure produced a reduction in the ash content from 0.20 weight percent to 0.16 weight percent based on the weight of the original drain oil.

In Example 5, the hydrocarbon diluent was deleted while increasing the quantity of the alcohol-water mixture and the ash content of the drain oil was reduced to 1.10 percent. Similarly, in Example 6, both the quantity of the drain oil and the hydrocarbon diluent were decreased while increasing the weight of the alcohol-water mixture and decreasing the quantity of the base.

TABLE III

Example No.	Drain Oil of 0.64% (wt.) Ash	
		7
Drain Oil (mls.)		25
Naphtha Diluent (mls.)		25
50% (vol.) Isopropyl Alcohol-Water (mls.)		50
Na ₂ CO ₃ (gm/100ml Alc-Water)		1
Recovery of Drain Oil-Vol.%		90
Ash of Recovered Drain Oil-Wt.%		0.12
Dispersion-Organic Layer		None
Dispersion-Alcohol Layer		None

Table III illustrates the results obtained in Example 7 where a used drain oil having an ash content of 0.64 percent by weight was treated. As shown, the ash content was reduced to 0.12 percent by weight of the treated oil and the separation between the organic layer and the alcohol layer was clean with no dispersion noted in either layer.

TABLE IV

Example No.	Drain Oil-1.73% (wt.) Ash (Dilution Effect)				
	8	9	10	11	12
Drain Oil (mls.)	100	66.7	50	33.3	20
Naphtha Diluent (mls.)	0	33.3	50	66.7	80
Recovery of Drain Oil-Vol.%	99.8	99.1	99.5	99.4	99.5
Ash of Recovered Drain Oil-Wt.%	1.60	1.30	1.22	1.11	0.90
Dispersion-Organic Layer	Yes	Yes	Yes	Yes	Yes

TABLE II

Example No.	Drain Oil of 1.65% (wt.) Ash			
	4(a)	4(b)	5	6
Drain Oil (mls.)	25	50	33.3	16.7
Naphtha Diluent (mls.)	25		0	16.7
50% (vol.) Isopropyl Alcohol-Water (mls.)	50	50	66.7	66.6
Na ₂ CO ₃ (gm/100ml Alc-Water)	1	1	1	0.5
Recovery of Drain Oil-Vol.%	98	98	98	97
Ash of Recovered Drain Oil-Wt.%	0.20	0.16	1.10	0.44
Dispersion-Organic Layer	None	None	None	None
Dispersion-Alcohol Layer	Yes	None	None	None

Table IV illustrates the effect of dilution, i.e., variations in the amount of hydrocarbon diluent with respect to the amount of drain oil, without a following treatment with an alcohol-water mixture. As shown in Example 8, some reduction in ash content was obtained merely by centrifuging the drain oil. As the quantity of hydrocarbon diluent was increased in Examples 9-12 while the quantity of drain oil was decreased, there was a continuing reduction in the ash content of the recovered drain oil. However, there was still a substantial amount of ash in the treated oil which indicates that dilution, while important, is not sufficient to purify the drain oil without the added step of contacting the diluted drain oil with the alcohol-water mixture which contains a base.

1.73 percent by weight of ash, it was observed that an isopropyl alcohol concentration of about 40 percent to about 50 percent by volume in the alcohol-water mixture

Table VI sets forth the results obtained in Examples 19-25 in which both the alcohol and the alcohol concentration in the alcohol-water mixture were varied. As illustrated, all of the various alcohols tested were found to be effective and, in addition to iso-propanol, *n*-propanol and tert-butanol were found to be particularly effective.

ture was most effective. Using these concentrations, there was a very marked reduction in the ash content of the treated oil and a very clean separation between the organic layer and alcohol layer. Surprisingly, at either higher or lower concentrations of isopropanol, the

TABLE V

Example No.	Drain Oil-1.73% (wt.) Ash Variation in Alcohol Concentration					
	13	14	15	16	17	18
Drain Oil (mls.)	25	25	25	25	25	25
Naphtha Diluent (mls.)	25	25	25	25	25	25
Vol.-% Isopropanol in Water	20	30	40	50	60	70
Isopropanol-Water (mls.)	50	50	50	50	50	50
Na ₂ CO ₃ (gm/100ml Alc-Water)	2	2	2	2	2	2
Recovery of Drain Oil-Vol. %	100	100	98	92	86	86
Ash of Recovered Drain Oil-Wt. %	0.89	0.69	0.31	0.29	0.53	0.51
Dispersion-Organic Layer	Yes	Some	None	None	None	Some
Dispersion-Alcohol Layer	None	None	None	None	None	Yes

Examples 13-18, shown in Table V, illustrate the effect of variations in the alcohol concentration of the alcohol-water mixture which was employed. For the particular drain oil undergoing treatment, which contained

process was less effective as evidenced by a higher ash content in the recovered oil and the formation of some dispersion in the organic layer or alcohol layer.

TABLE VI

Example No.	Drain Oil-1.73% (wt.) Ash Variations in Alcohol and Alcohol Concentration						
	19	20	21	22	23	24	25
Drain Oil (mls.)	25	25	25	25	25	25	25
Naphtha Diluent (mls.)	25	25	25	25	25	25	25
Alcohol	Methanol	Ethanol	Ethanol	Ethanol	<i>n</i> -Propanol	Sec-Butanol	Tert-Butanol
Vol.-% Alcohol in Water	50	40	50	60	50	20	50
Alcohol-Water (mls.)	50	50	50	50	50	50	50
Na ₂ CO ₃ (gm/100ml Alc-Water)	1	1	1	1	1	1	1
Recovery of Drain Oil-Vol. %	140	94	128	132	94	106	106
Ash of Recovered Drain Oil-Wt. %	1.2	0.65	0.66	1.7	0.24	0.71	0.28
Dispersion-Organic Layer	Yes	Some	Yes	Yes	None	Yes	None
Dispersion-Alcohol Layer	None	Yes	Yes	Yes	None	Yes	None

TABLE VII.-DRAIN OIL-1.73 PERCENT (WT.) ASH VARIATION IN BASE

Example No.	26	27	28	29	30	31	32	33	34	35	36
Drain oil (mls.)	25	25	25	25	25	25	25	25	25	25	25
Naphtha diluent (mls.)	25	25	25	25	37	25	25	25	25	25	25
Vol. percent isopropanol in water.	50	50	50	40	60	50	50	50	50	50	50
Isopropanol-water (mls.)	50	50	50	50	50	50	50	50	50	50	50
Base (1.0 gm. / 100 ml. alc-water)	NaHCO ₃	Na ₂ SO ₄	(NH ₄) ₂ CO ₃	(NH ₄) ₂ CO ₃	(NH ₄) ₂ CO ₃	Na ₃ PO ₄	Na ₂ HPO ₄	Na ₂ CO ₃	K ₂ CO ₃	Li ₂ CO ₃	NaOH
Recovery of drain oil-vol. percent.	90	96	90	82	94	70	90	92	80	86	64
Ash of recovered drain oil-wt. percent.	0.81	0.81	0.66	0.93	0.67	0.38	0.47	0.30	0.33	0.89	0.85
Dispersion-organic layer	None	None	None	None	None	Haze	Haze	None	None	Some	Some
Dispersion-alcohol layer	Yes	Yes	Yes	Yes	Yes	Yes	Yes	None	Some at Interface	Yes	Yes

Table VII describes the results obtained in Examples 26-36 in which various bases were employed in the alcohol-water mixture. As shown, all of the bases which were tested were found to be effective and the alkali metal carbonates and phosphates were particularly effective.

amples, a variety of diluents may be employed in the present process, ranging from aliphatics to aromatics and including a dehydrated overhead from a used drain oil.

In order to ascertain the nature of the metals found in used lubricating oils, and the effectiveness of the

TABLE VIII

Example No.	Drain Oil-1.73% (wt.) Ash Variation in Diluent				
	37	38	39	40	41
Drain Oil (mls.)	25	50	25	25	50
Hydrocarbon Diluent	Kerosene	Xylene	Xylene	Dehydrated Overhead	Dehydrated Overhead
Diluent (mls.)	25	50	25	25	50
50% (vol.) Isopropyl Alcohol-Water (mls.)	50	0	50	50	0
Na ₂ CO ₃ (gm/100ml Alc-Water)	1	0	1	1	0
Recovery of Drain Oil-Vol.%	82	96	98	100	
Ash of Recovered Drain Oil-Wt.%	0.24	0.94	0.26	0.26	0.92
Dispersion-Organic Layer	None	Yes	None	None	Yes
Dispersion-Alcohol Layer	None		None	None	

Table VIII illustrates the results obtained from Examples 37-41 in which the hydrocarbon diluent was varied. In Example 37, 25 mls. of kerosene was utilized as the diluent and the drain oil, after treatment, had an ash content of 0.24 percent by weight based on the used oil. In Example 38, xylene was employed as a diluent, but the diluted drain oil was not contacted with a water-alcohol mixture as required in the process. As illustrated, xylene, while a good diluent, was not effective to produce the desired reduction in the ash content of the oil in the absence of the contacting step with a water-alcohol mixture.

In Example 39, xylene was used as the diluent and the diluted oil was then treated with an alcohol-water mixture in accord with the process. This provided a reduction in the ash content to 0.26 percent.

Examples 40 and 41 demonstrate the use of a dehydrated overhead from a drain oil as the hydrocarbon diluent. In Example 40 with contact of an alcohol-water mixture containing a base, the ash was reduced to 0.26 percent based on the used oil being treated. In Example 41, the mixture of overhead and drain oil was centrifuged but the diluted oil was not contacted with the alcohol-water mixture. As expected, Example 41 demonstrates that simple dilution with the hydrocarbon diluent was not effective in reducing the ash content to the desired levels.

TABLE IX

Properties	Characteristics of Hydrocarbon Diluents			Xylene
	Kerosene	Naphtha	Dehydrated Overhead	
Gravity, °API	41.5	47.3	45.0	31.3
Reid Vapor Pressure		0.3	1.5	
Sulfur, % by wt.	<0.01	<0.01	0.1	<0.01
Flash Point, Tag				
Closed Cup—°F.	152	104	60	83
Distillation				
Initial Boiling Pt., °F.	380	311	180	283
End Point, °F.	499	386	480	293

Table IX illustrates the characteristics of the hydrocarbon diluents referred to in the various examples previously described. As indicated by Table IX and the ex-

present process in reducing the content of these metals, the metals analysis set forth in Table X was conducted on a drain oil in its as is condition and on the purified drain oil after treatment according to the present process. The used drain oil, which was employed in a number of the previously described examples, contained 1.73 percent by weight of ash while the purified oil was obtained using the process conditions set forth in Example 33. The metals content shown for the purified oil is corrected to the weight of the used oil in the same manner as described previously.

TABLE X

Element	Metals Content of Drain Oil in Parts Per Million	
	Original Drain Oil 1.73% (wt.) Ash	Treated Oil Example 33
Lead	5,000	180
Zinc	1,500	210
Phosphorus	860	260
Calcium	1,500	110
Iron	390	120
Magnesium	420	50
Barium	440	130
Potassium	230	10
Sodium	20	250
Others (Cr, Sb, Cd, Sn, B, Mn, Cu, Ni, Al, Bi, Mo, Li, Ag, Ti)	210	50
Total	10,570	1,379

As indicated in the above table, the present process was effective in reducing the content of all the various metals found in drain oil. As would be expected, there was an increase in the sodium content of the oil resulting from the process conditions of Example 33 in which the base present in the alcohol-water mixture contained sodium. The tremendous reductions in the metals content of the oil shown in Table X, which parallel closely the reduction in the ash content of the treated oil based on the weight of original oil, demonstrate the worth of the process in recovering valuable metals, as well as in recovering valuable high viscosity index oils.

The presence of metals in a used lubricating oil makes the oil very difficult to treat by conventional refining processes. By greatly reducing the metals con-

tent of a used lubricating oil in accord with the present process, the resulting oil may then be treated further using conventional refinery processing, such as distillation, hydrotreating, etc.

As illustrated by the foregoing discussion and the Examples, the present process provides a solution to the longstanding problem of recycling used lubricating oils. Thus, the use of the process will make a substantial contribution to environmental quality by providing a reduction in pollution of the air or water from the burning or disposal of used lubricating oils. Further, the present process represents a substantial contribution to the conservation of natural resources since it enables the reuse of relatively scarce high viscosity index oils which are needed for automotive lubrication.

We claim:

1. A method of purifying a used lubricating oil comprising:

admixing the used lubricating oil with a mutually soluble predominantly hydrocarbon liquid diluent having a boiling range within the temperature region of about 100°F. to about 500°F.;

admixing the diluted lubricating oil with a water-miscible alcohol and water mixture containing a small amount of an ammonium or alkali metal base; and

centrifuging to remove sludge and metal compounds from the oil and to separate the diluted oil phase from the alcohol-water phase.

2. The method of claim 1 wherein the ratio of the predominantly hydrocarbon liquid diluent with respect to the used lubricating oil being treated ranges from about 2:1 to about 1:2 by volume.

3. The method of claim 1 wherein the quantity of the ammonium or alkali metal base is sufficient to displace polyvalent metal ions from the various metallic soaps contained in the used lubricating oil undergoing treatment.

4. The method of claim 2 wherein the water-miscible alcohol is methanol, ethanol, isopropyl alcohol, *n*-propyl alcohol, sec-butyl alcohol or tert-butyl alcohol.

5. The method of claim 2 wherein the water-miscible alcohol is isopropyl alcohol, tert-butyl alcohol or *n*-Propyl alcohol.

6. The method of claim 5 wherein the water-miscible alcohol-water mixture contains from about 40 percent to about 60 percent by volume of the alcohol.

7. The method of claim 2 wherein about one-half to about one volume of the water-miscible alcohol-water mixture are employed for each volume of the diluted lubricating oil.

8. The method of claim 4 wherein about one-half to about one volume of the water-miscible alcohol-water mixture are employed for each volume of the diluted lubricating oil.

9. The method of claim 5 wherein about one-half to about one volume of the water-miscible alcohol-water mixture are employed for each volume of the diluted lubricating oil.

10. The method of claim 6 wherein about one-half to about one volume of the water-miscible alcohol-water mixture are employed for each volume of the diluted lubricating oil.

11. The method of claim 1 wherein the base is sodium carbonate, potassium carbonate, or sodium phosphate.

12. The method of claim 5 wherein the base is sodium carbonate, potassium carbonate, or sodium phosphate.

13. The method of claim 9 wherein the base is sodium carbonate, potassium carbonate, or sodium phosphate.

14. The method of claim 1 including the steps of: distilling the diluted oil phase obtained from the centrifuging to obtain a light naphtha cut, and recycling the light naphtha cut to the process for use as the predominantly hydrocarbon liquid diluent.

15. A method of purifying a used lubricating oil comprising:

admixing the used lubricating oil with a mutually soluble predominantly hydrocarbon liquid diluent with the volume ratio of liquid diluent to used lubricating oil ranging from about 2:1 to about 1:2 and the liquid diluent having a boiling range within the temperature region of about 100°F. to about 500°F.;

admixing the diluted lubricating oil with a mixture of isopropyl alcohol, *n*-propyl alcohol, or tert-butyl alcohol and water which contains a small amount of an ammonium or alkali metal base with about one-half to about one volume of the alcohol-water mixture being employed for each volume of the diluted lubricating oil, and

centrifuging to remove sludge and metal compounds from the oil and to separate the diluted oil phase from the alcohol-water phase.

16. The method of claim 15 wherein the alkali metal base is sodium carbonate, potassium carbonate, or sodium phosphate.

17. The process of claim 16 wherein the quantity of the base is sufficient to displace the polyvalent metal ions from the various metallic soaps contained in the used lubricating oil undergoing treatment.

18. The process of claim 15 wherein the alcohol-water mixture contains from about 40 to about 60 percent by volume of alcohol.

19. The method of claim 1 wherein said alcohol is a mixture of water miscible alcohols.

20. A method of purifying a used lubricating oil comprising:

admixing the used lubricating oil with a mutually soluble predominantly hydrocarbon liquid diluent; admixing the diluted lubricating oil with a water-miscible alcohol and water mixture containing a small amount of an ammonium or alkali metal base, and

centrifuging to remove sludge and metal compounds from the oil and to separate the diluted oil phase from the alcohol-water phase.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,819,508

Dated June 25, 1974

Inventor(s) Morton Fainman and Charles Strouse McAuley

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The designation of inventors in item [76] of the cover sheet is in error in that the name appearing as Charles Strouse "McCauley" should be changed to read Charles Strouse --McAuley--.

Signed and sealed this 8th day of October 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents