

[54] **RECLAIMING USED MOTOR OIL BY
CHEMICAL TREATMENT WITH
AMMONIUM PHOSPHATE**

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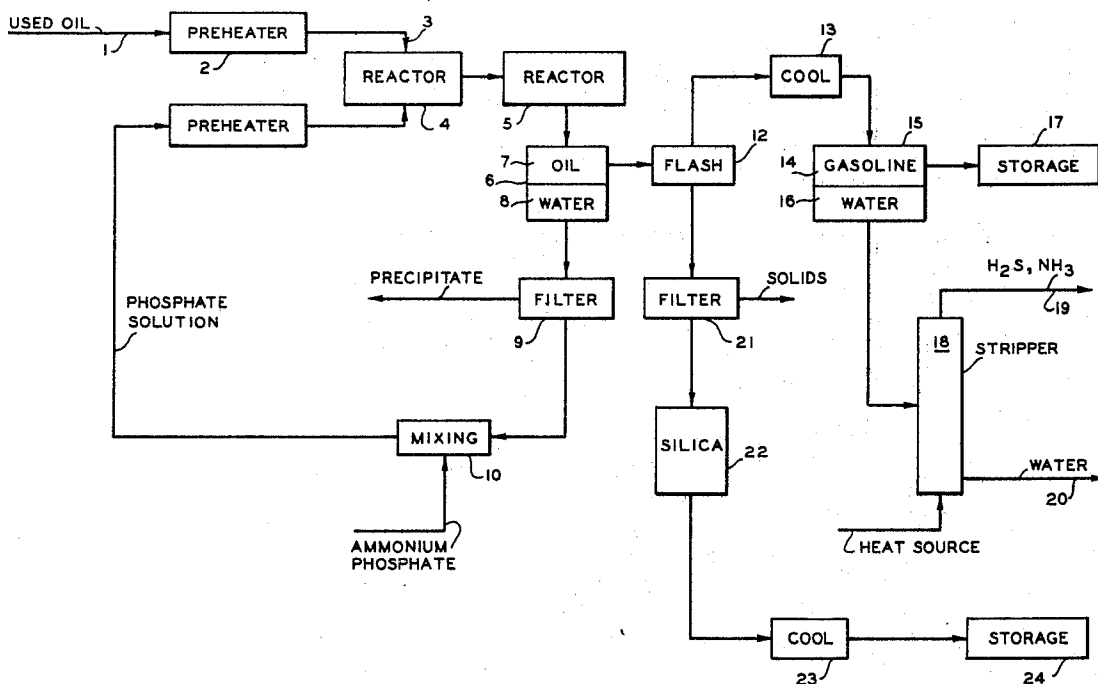
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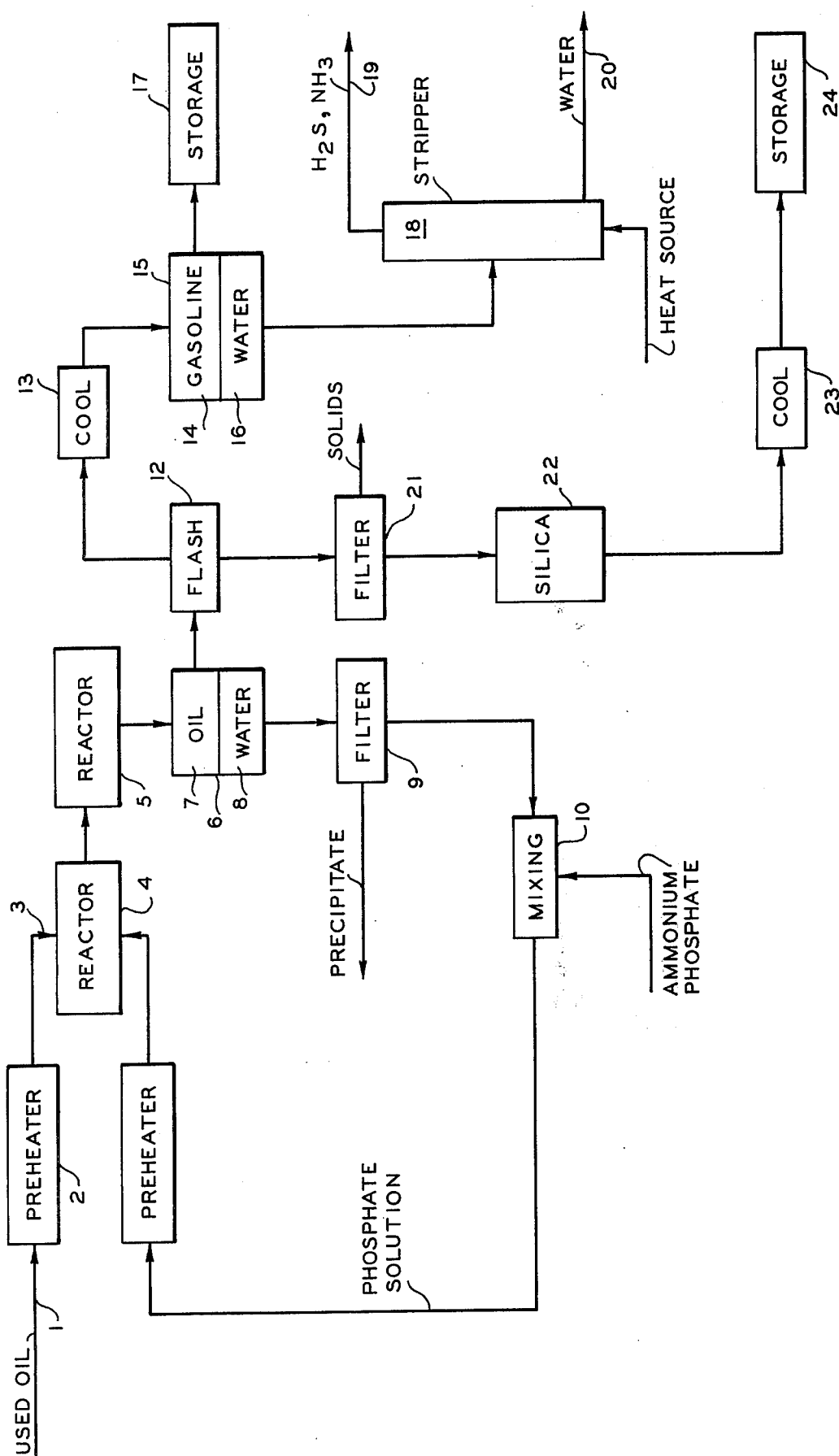
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ABSTRACT

A method is provided for reducing the ash content and the lead content of used motor oil by contacting the used oil with an aqueous solution of an ammonium phosphate. In one embodiment of the invention a used motor oil is treated in an integrated ecological method for removal of contained metal salts, tetraethyllead, gasoline, ammonia, and hydrogen sulfide so that removal of each of these contaminants can be accomplished without contaminating the environment by returning the removed components to the environment.

10 Claims, 1 Drawing Figure





RECLAIMING USED MOTOR OIL BY CHEMICAL TREATMENT WITH AMMONIUM PHOSPHATE

BACKGROUND OF THE INVENTION

This invention relates to treatment of motor oils. In one of its aspects this invention relates to the removal of impurities of used motor oil. In another of its aspects this invention relates to an ecological method for removing contaminants from a used motor oil. In more specific aspects of the invention it relates to the reduction of ash content and lead content in a used motor oil. In still another aspect of the invention it relates to the removal and separation of such specific contaminants as gasoline, metal salts, tetraethyllead, ammonia and hydrogen sulfide in a process for treating used motor oil.

In one of its concepts this invention relates to the reduction or removal of contaminants from a used motor oil by a series of treatments of the motor oil, the treating reagent, and product stream so that all process streams are either recycled or can be removed under conditions to avoid contamination of the environment.

In view of the increasing concern regarding conservation of our petroleum reserves and the best use of products derived from them this invention is of timely significance. Oil purified by the practice of this invention can be used as a burning oil substantially free of the harmful lead and other additives of modern lubricating oils. Thus, atmospheric pollution is reduced by utilizing the purified oil as a burning stock. Conservation is achieved by reuse of the oil that would otherwise be discarded. The purified oil now free of metal contaminants can be reprocessed by means of conventional hydrotreating processes to yield a high grade lubricating oil-based stock that can be recompounded to give high grade lubricating oil. Alternately, the purified oil can be used for road oil or heating oil, if desired.

The process by which the used motor oil is purified is also designed to recirculate the processed material and to remove compounds potentially hazardous to the environment in such a way that no ecological problem is produced. It is therefore an object of this invention to provide a method for reducing the ash content and the lead content of used motor oil. It is another object of this invention to provide a method for treating used motor oil so that metal salts, tetraethyllead, gasoline, ammonia, and hydrogen sulfide that can be removed in the process of this invention are handled in such a manner that ecological hazards can be avoided.

Other aspects, objects and the advantages of this invention will be apparent to one skilled in the art upon studying the specification, drawing and the appended claims.

SUMMARY OF THE INVENTION

In accordance with the invention a method for reducing the ash content of used motor oil is provided in which the used oil contacted with an aqueous solution of ammonium phosphate reagent under conditions that will react the ammonium phosphate with metal salts present in the used oil thereby forming a precipitate of metal salt compounds which will settle in the water layer produced in the reaction leaving an oil layer substantially reduced in ash producing contaminants. Similarly, this process reduces the lead content of the used oil by reaction of the lead salts with the ammonium

phosphate reagent to produce lead compounds that will precipitate from the reaction solution.

In another embodiment of the invention an integrated process is provided in which used motor oil is preheated and intermixed in at least one stirred reactor with a heated aqueous solution of an ammonium phosphate to produce precipitable metal compounds. These metal compounds precipitate from the hot reaction mixture and are allowed to settle in the water layer as the oil and water separate into separate layers. The water layer is then filtered to remove the precipitate, ammonium phosphate is added to this filtered water and recirculated through a preheater to the reaction. The oil layer is flashed to remove gasoline and water that are present in the oil. The gasoline and water mixture is cooled and allowed to separate into a gasoline layer and a water layer. The gasoline layer is then pumped to storage while the water layer is stripped by a standard heated distillation process to remove hydrogen sulfide and ammonia that may be present with recovery of the hydrogen sulfide and ammonia and recycle of the water to the reaction process or discarding of the water. The flashed oil is filtered and passed through a heated silica gel treatment to remove tetraethyllead. The oil is then optionally cooled and passed to a storage chamber.

The basis for the recovery process of this invention is the discovery that ammonium phosphates are particularly suitable for reacting with metal salts usually contained in used motor oil to produce insoluble salts that will precipitate from the oil. Ammonium phosphate suitable in the practice of the invention include triammonium phosphate, diammonium hydrogen phosphate, ammonium dihydrogen phosphate and mixtures thereof. The concentration of the salt or salts in aqueous solution can vary broadly from about 2 to about 25 weight percent. On a practical basis it has been found that a concentration of the phosphate salt in aqueous solution of about 5 to about 15 weight percent is preferred.

Reactor conditions required for carrying out the reaction are as follows: The pressure can vary from about atmospheric to about 750 psig. Although, the reaction is preferably run at about 90 to about 350 psig, as stated above, the reaction of the invention will take place by contact of the reactant motor oil and the ammonium phosphate at about atmospheric pressure. The temperature suitable for carrying out the reaction can vary from about 200° to about 500°F, again, for practical considerations, the preferable temperature range is from about 325° to about 425°F.

The used motor oils treated by the process of this invention are primarily the discarded oils that have been used for automotive lubrication purposes such as crankcase oils, transmission and gear oils and the like. Other sources of used oils include steam-turbine oils, steam-engine oils, hydraulic oils, heat-transfer oils, cutting oils and the like.

The oils used for the purposes named above are the refined lubricating cuts from paraffin-base, mixed-base, or naphthenic crudes. Their viscosities are generally in the range of from about 100 to 1,800 SUS at 100°F. The oils also contain various additives such as oxidation inhibitors (i.e. barium, calcium and zinc alkyl thiophosphates, di-t-butyl-p-cresol, etc.), antiwear agents (i.e. organic lead compounds such as lead diorganophosphorodithioates, zinc dialkylidithiophos-

phates, etc.), rust inhibitors (i.e. calcium and sodium sulfonates, etc.), dispersants (i.e. calcium and barium sulfonates and phenoxides, etc.), viscosity index improvers, [i.e. polyisobutylenes, poly (alkylstyrenes), etc.], detergents (i.e. calcium and barium salts of alkyl benzene sulfonic acids and ashless type detergents such as alkyl-substituted succinimides, etc.

Synthetic oils such as the diesters derived from adipic, azelaic or sebacic acids esterified with C_8 to C_{18} branched-chain alcohols used for lubricating purposes exemplified by di(2-ethylhexyl) sebacate, di(3,5,5-trimethylhexyl) adipate, di(3,7-dimethyloctyl) azelate and the like can also be reclaimed by the process of the invention using the milder conditions to avoid degradation of the oils by hydrolysis.

The following example is offered as an illustration of the effectiveness of ammonium phosphate reagents in reducing the ash content and inorganic lead content of used motor oil. Sources of the inorganic lead include degraded tetraethyllead from burned gasoline, worn bearing material, degraded organic lead additives in the oil and the like. The example should be taken as illustrative and not restrictive.

EXAMPLE I

In a series of autoclave tests in triplicate, 100 ml of used detergent-containing, multi-grade motor oil containing conventional additives taken from a car after 6,000 miles of use was added to a 300 ml autoclave containing 30 ml of water and 3 grams of a phosphate reagent as described below. The sealed autoclave was heated to about 370°F (i.e. range was 366°–375°) and stirred for one hour after which the contents were allowed to settle for 10 minutes. The pressure was measured at 170 psig. The oil layer was separated by a dip tube above the aqueous layer and analyzed for ash content. The results are given in Table I.

Table I

Effect of Phosphate Reagents on Ash Removal

Reagent	Ash Content Wt. %	Inorganic Lead Content Wt. %
none	3.11	0.95
ortho phosphoric acid ^a	0.48	— ^c
ammonium dihydrogen phosphate	0.10	< 0.01
diammonium hydrogen phosphate	0.12	< 0.01
trisodium phosphate ^b	5.00	— ^c

^aOil phase allowed to settle an additional 48 hours before analysis.

^bIntractable emulsion at 366°F; some phase separation after 16 hours. Analysis performed after product stood 16 hours at room temperature.

^cNot run since excessive amount of ash is present.

Examination of the results shows that ammonium phosphates give effective removal of ash components with the insoluble metal phosphates formed settling rapidly in the water phase where they are collected. With phosphoric acid the reaction is not complete and it is difficult to separate the aqueous and oil phases. With trisodium phosphate a stable emulsion is formed even at 370°F. The ammonium phosphate treatment reduced the inorganic lead content to less than 0.01 weight percent which corresponds to removal of about 98 percent or better of the inorganic lead originally present.

At the elevated temperatures used in the process, the ammonium salts of organic acids are not stable; the equilibrium lies in the direction of ammonia and the organic acid which is oil soluble. The organic acids result from the conversion of the heavy metal salts of the or-

ganic acids used as additives in modern lubricating oils due to the ammonium phosphate treatment. Thus, organic acids are not extracted to any marked extent into the water phase with ammonium phosphates. Sodium phosphates give the water soluble sodium salts of organic acids and should be avoided in processes directed at ash removal for preparing a fuel or road oil. The removal of organic acids and petroleum sulfonates as water soluble sodium salts complicates the water reuse or disposal problem as the data tabulated for trisodium phosphate in Table I demonstrates.

The embodiment of the invention presenting an integrated ecological system for treating used motor oils can best be understood in conjunction with the drawing which illustrates in schematic diagram a process for treating used motor oil with recycle or recovery of various treating and treated components.

Referring now to the drawing, used oil can be passed through line 1 to a preheater 2 where the temperature is raised from about 200° to about 500°F and in one embodiment from about 325° to about 425°F. The preheated oil is passed through line 3 into the first of a series of stirred reactors 4 where it is contacted with an aqueous solution of ammonium phosphate which has been preheated to a temperature in the same range. The pressure in the reactors and in the oil-water separator is sufficient to maintain the reaction mixture substantially completely in the liquid phase. In the reactor, the mixture is agitated vigorously. The reaction mixture can then be passed to another stirred reactor 5 where the same reaction conditions and agitation are maintained.

The reaction mixture is passed to a phase separator 6 in which the oil layer 7 and the water layer 8 are allowed to separate. During this separation precipitated

metal salts rapidly settle into the water layer.

The water layer with precipitate is passed through a filter 9 where the precipitate is removed and discarded or processed to recover the metal or metals contained therein. The filtered water is then admixed with ammonium phosphate in 10 to bring the concentration of ammonium phosphate into the range of about 5 to about 15 weight percent and recycled to a preheater 11 where the temperature is raised within the reaction range and the material passed back to reactor 4. By maintaining the phase separation, filtering of the water, and the addition of ammonium phosphate at temperatures somewhat reduced from the reaction temperature the filtering operation and the dissolving of the ammonium phosphate are facilitated and a minimum of preheat is required in preheater 11. Heating or cooling are adjusted as required to meet these objectives.

The oil layer 7 from phase separator 6 is passed into a flash chamber 12 where the pressure is reduced to atmospheric or slightly above and the gasoline and water present in the oil are flashed to a vapor. This vapor is then cooled in a cooler 13 to a temperature sufficiently low to condense the gasoline and water at the pressure in the vessels. Cooled liquid is passed to a phase separator 14 where a gasoline layer 15 and a water layer 16 are allowed to form. The gasoline layer can then be transferred to storage 17 and the water layer 16 can be passed to a stripping operation 18 operated at conditions, such as temperature, pressure, flow rate, etc., well known in the art, sufficient to remove ammonia and hydrogen sulfide as overhead product 19. These products can then be recovered or destroyed.

The stripped water 20 from the stripper 18 can then be recycled for use in the aqueous ammonium phosphate system or, at this point in the operation, is sufficiently free from harmful contaminants to be discarded into the environment. Any convenient heat source such as hot flue gases from the preheaters can be used for operating the stripping system.

The oil layer 7 which has been flashed is passed, while still close to reaction temperature, through a filter 21 to remove extraneous matter and then through a bed of silica gel 22 at a temperature above 350°F to remove the tetraethyllead. Tetraethyllead (TEL) in the oil resulting from contamination with gasoline containing it is not removed by the ammonium phosphate treatment. For example, an autoclave test with gasoline containing TEL did not show a change in lead content on heating to 370°F for 1 hour with an aqueous solution of ammonium phosphate. However, it is known from U.S. Pat. No. 2,745,793 that TEL is removed from hydrocarbons such as gasoline by passing the gasoline through a bed of silica gel at temperatures above 350°F. A similar effect is expected with the TEL present in used motor oil, giving a product containing very little alkyl lead. The treated oil is then optionally cooled by heat exchange with a cooling medium 23 and passed to storage 24 or simply passed directly to storage 24.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, the drawing and the appended claims of the invention, the essence of which is that there has been provided a method for treating used motor oil with ammonium phosphate compounds whereby the ash content and lead content of the used oil is reduced sufficiently to allow reuse of the used motor oil.

I claim:

1. A method for reducing the ash content of used motor oil said method comprising (a) contacting said used oil with an aqueous solution of an ammonium phosphate reagent at conditions of temperature and pressure sufficient to react said ammonium phosphate with metal salts present in the used motor oil, (b) allowing the precipitate formed by the reaction to settle, and (c) separating the oil from the water and solid precipitate.

2. A method of claim 1 wherein the ammonium phosphate is chosen from among triammonium phosphate, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, and mixtures thereof.

3. A method of claim 1 wherein the reaction temper-

ature is in the range of about 200° to about 500°F, the reaction pressure is in the range of about atmospheric to about 750 psig, and the concentration of ammonium phosphate in the aqueous reaction solution is about 2 to about 25 weight percent.

4. A method for reducing the lead content of used motor oil, said method comprising: (a) contacting said oil with an aqueous solution of ammonium phosphate reagent at conditions of temperature and pressure sufficient to react said ammonium phosphate with lead compounds present in the used motor oil, (b) allowing the precipitate formed by the reaction to settle, and (c) separating the oil from the water and solid precipitate.

5. A method of claim 4 wherein the ammonium phosphate is chosen from among triammonium phosphate, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, and mixtures thereof.

6. A method of claim 4 wherein the reaction temperature is in the range of about 200° to about 500°F, the reaction pressure is in the range of about atmospheric to about 750 psig, and the concentration of ammonium phosphate in the aqueous reaction solution is about 2 to about 25 weight percent.

7. A method for reclaiming used motor oil containing metal salts, said method comprising: (a) preheating the used motor oil to a temperature in the range of 200° to about 500°F, (b) preheating an aqueous solution of ammonium phosphate to a temperature in the range of about 200° to about 500°F, (c) contacting said preheated motor oil and said preheated aqueous solution of ammonium phosphate in at least one agitated reactor at conditions sufficient to maintain a reaction producing a precipitate, (d) allowing the reaction product to separate into an oil layer and a water layer and the precipitate to settle in the water layer (e) removing the water layer and filtering the precipitate from the water, (f) adding sufficient ammonium phosphate to the filtered water to produce an aqueous solution of ammonium phosphate having a concentration of about 2 to about 25 weight percent ammonium phosphate and recirculate through the preheater in (b), and (g) removing the oil.

8. A method according to claim 7 wherein said used motor oil also contains tetraethyllead, said method comprising: (a) obtaining a treated oil containing tetraethyllead by the method of claim 7, and (b) passing said treated oil through silica gel at a temperature above 350°F, thereby removing the tetraethyllead, and (c) recovering the further treated oil.

9. A method of claim 7 wherein said used motor oil also contains gasoline, said method comprising: (a) obtaining a treated oil by the method of claim 7, (b) flashing the oil-gasoline mixture to remove from the oil any gasoline and water that has been retained in the oil, (c) separating the water and gasoline, and (d) recovering the gasoline, oil, and water as separate products.

10. A method of claim 9 wherein said treated motor oil also contains hydrogen sulfide and ammonia, said method comprising: (a) obtaining flashed water containing hydrogen sulfide and ammonia by the method of claim 9, (b) stripping said water to remove hydrogen sulfide and ammonia, and (c) recovering hydrogen sulfide, ammonia, and water as separate products.

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