Dec. 1, 1959 I. W. MILLS ET AL 2,915,460

REFINING MINERAL OIL

Filed Dec. 30, 1954

Fig. 1

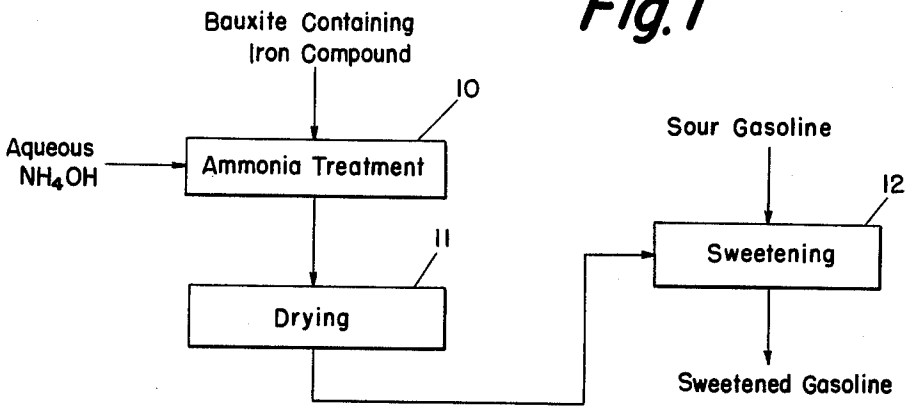
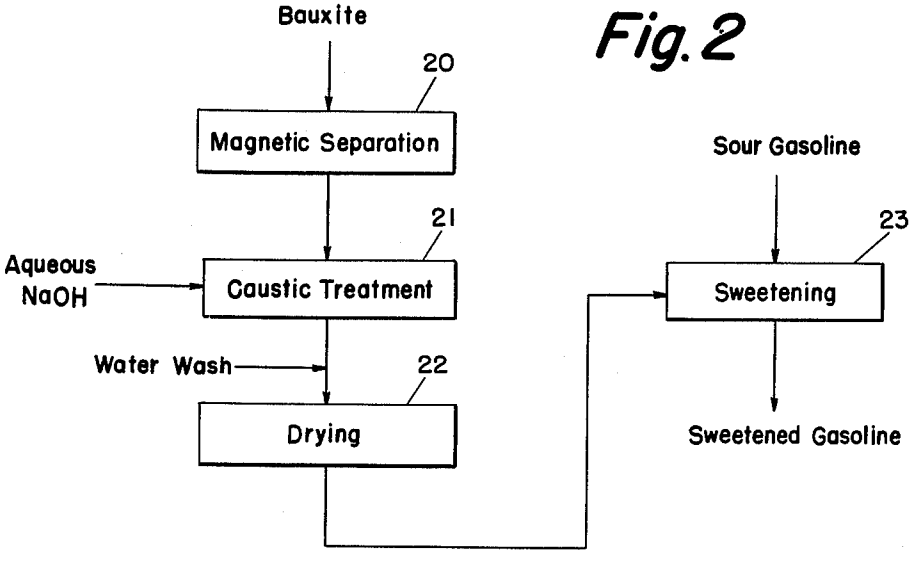


Fig. 2



INVENTORS.
IVOR W. MILLS
PETER B. MURRAY
BY
Robert O. Spindle
ATTORNEY

United States Patent Office 2,915,460
Patented Dec. 1, 1959

2,915,460

REFINING MINERAL OIL

Ivor W. Mills, Glenolden, and Peter B. Murray, Media, Pa., assignors to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

Application December 30, 1954, Serial No. 478,768

15 Claims. (Cl. 208—189)

This invention relates to the refining of mineral oil and more particularly to the conversion or removal of mercaptans and other objectionable sulfur compounds from mineral oil.

Various means have been proposed for converting or removing mercaptans from various mineral oil fractions such as gasoline, naphtha, etc., and some of the means which have been proposed may produce a product having satisfactorily low mercaptan content, but the life of the treating agent which is used may be unsatisfactorily short.

It is possible, employing bauxite or other adsorbents, to reduce the mercaptan content of mineral oil fractions to a qute low level, but after a certain amount of mineral oil has been contacted with a given portion of bauxite, the activity of the latter for reducing mercaptan content becomes decreased. Upon decrease of the bauxite activity, the mineral oil products obtained subsequently from that bauxite will contain unsatisfactorily large amounts of mercaptans.

According to the invention, a process for reduction of mercaptan content, employing an adsorbent, is provided wherein the life of the adsorbent is substantially increased. This makes it possible to treat mineral oil for substantially longer periods before having to regenerate or discard the adsorbent.

The process of the invention is applicable to those adsorbents which contain iron or iron compounds. The process of the invention involves the treatment of the adsorbent with an alkali prior to the use of the adsorbent as a sweetening agent for mineral oil.

Alkalis, for the purpose of the present invention, are considered to include ammonia, ammonium hydroxide, ammonium carbonate, and the alkali metal hydroxides and carbonates, e.g. sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, etc. Generally, aqueous solutions of alkalis will be employed in treating adsorbents according to the invention, but gaseous ammonia can also be employed.

It has been found that treatment of adsorbents with alkalis as subsequently more fully described, considerably increases the ability of the adsorbent to reduce the mercaptan content of hydrocarbon materials.

The invention will be further described with reference to the attached drawings. Figure 1 is a schematic flow sheet of one embodiment of the process according to the invention. Figure 2 is a schematic flow sheet of another embodiment.

Referring to Figure 1, bauxite containing iron compounds is introduced into ammonia treating zone **10**. The bauxite which is introduced may be a bauxite which has not been given any prior treatment other than the customary thermal activation, e.g. at a temperature of 600–700° F. or higher, and which contains substantial amounts of iron oxide, generally within the range from 1 to 25 percent, for example about 15 percent; other iron compounds may also be present. Alternatively the

bauxite introduced into zone **10** may have been treated in any known manner to reduce the iron content. It is to be noted however that preferably the iron content of the bauxite employed is high, and therefore it is not preferred to use a bauxite which has been treated for reduction of iron content.

The bauxite introduced in zone **10** may have been treated beforehand to increase the iron content, for example by contacting the bauxite with an aqueous solution of an iron salt, e.g. ferrous or ferric chloride, sulfate, acetate, etc., preferably though not necessarily having at least 10 weight percent concentration, followed by evaporation of water from the impregnated bauxite.

Aqueous ammonium hydroxide is introduced into zone **10** and is contacted therein with the bauxite. The contacting may be accomplished for example by percolating an aqueous solution of ammonium hydroxide through a stationary bed of granular bauxite. The bauxite is subsequently dried in any suitable manner, as indicated by the drying zone **11**. In practice it is not necessary to transfer the bauxite from one zone to another as indicated in the drawing. Instead a stationary bed of bauxite which has been treated with ammonium hydroxide may be subsequently dried by blowing heated gases, e.g. air, through the bed of bauxite.

In the drying operation excess water is removed from the bauxite, and also excess ammonia is removed. It is not essential to this embodiment of the process of the invention that ammonia be present during the sweetening operation. It appears rather that the ammonia merely has the effect of converting the iron in the adsorbent to a different and superior form.

The conditions employed in the drying operation generally involve the use of a temperature within the approximate range from 150° F. to 600° F., preferably 200° F. to 400° F., for a sufficient period of time to obtain equilibrium at the temperature employed; the temperature employed should be above the boiling point of water at the pressure employed. The drying can for example be performed at atmospheric pressure or under vacuum conditions, e.g. at an absolute pressure less than about 100 mm. Hg. The water removed by such drying is mainly or entirely of the type generally known as free moisture, rather than the combined water which may be removed upon ignition of the bauxite.

Sour gasoline containing mercaptans or other objectionable sulfur compounds is sweetened by contact with the bauxite which has been treated with ammonia and dried; the sweetening operation is indicated at zone **12**. Here again it is not necessary to transfer the bauxite from one zone to another; instead the gasoline can be percolated through the same stationary bed of bauxite, after the termination of the drying operation.

Preferred conditions for the sweetening operation involve the use of atmospheric temperature and pressure. Elevated temperatures can be employed if desired, for example up to 250° F. However such elevated temperatures are not necessary for efficient reduction of mercaptan content, and may have an adverse effect upon the gum rating of the product obtained in the sweetening operation, particularly in the case of a cracked charge stock.

It is believed that the process of the invention involves not merely physical adsorption of constituents of the charge on the adsorbent, but an oxidation of mercaptan constituents, and that the presence of oxygen is therefore required during the contact of adsorbent with hydrocarbon material. Frequently the latter will contain sufficient oxygen, in the form of air, without employing any additional oxygen. If additional oxygen is needed, it may be added to the hydrocarbon material prior to the

adsorbent treatment, or introduced directly into the treating zone.

The sweetened gasoline product removed from zone 12 has a considerably lower mercaptan content than the original sour gasoline. It has been found for example that a doctor sweet product or a product having mercaptan content of 0%, as measured by the amount of a standard aqueous solution containing copper ions which reacts with the gasoline product, can be obtained.

In place of ammonium hydroxide, gaseous ammonia can be used in the treatment of the adsorbent prior to its use in sweetening.

Referring to Figure 2, thermally activated granular bauxite containing for example about 15 weight percent of iron compounds as Fe_2O_3 is introduced into a magnetic separation zone 20 wherein a process, as well known in the art, for magnetically separating bauxite particles having high iron content from bauxite particles having lower iron content is performed. The high iron bauxite, containing for example about 50 weight percent of iron compounds as Fe_2O_3, is introduced into caustic treatment zone 21 wherein the bauxite is contacted with caustic soda under conditions producing a substantial improvement in the sweetening ability of the high iron bauxite without destroying the essential granular structure or mechanical strength of the bauxite. In the light of the present specification, such conditions can readily be chosen by a person skilled in the art. The strength and amount of caustic employed and the temperature and time of the treatment are factors for which, because of their interdependence, absolute limits cannot be set. Preferably, the amount of caustic used is less than the stoichiometric amount for reaction with the alumina of the bauxite; more preferably, the amount of caustic employed is about 0.5 to 2 moles of caustic per mole of alumina in the bauxite. Also, preferably, the time of contact between caustic and bauxite is less than about one hour.

Following the caustic treatment, the excess sodium hydroxide is removed from the bauxite, e.g. by washing with water until the pH of the effluent wash water is less than 8 and preferably about 7. Excess water is then removed, in zone 22 as indicated in Figure 2. The conditions of the drying are generally similar to those described in connection with zone 11 of Figure 1.

The resulting bauxite is then used in zone 23 for sweetening sour gasoline under conditions generally similar to those described in connection with zone 12 of Figure 1.

The following examples illustrate the invention:

Example I

A series of runs was carried out wherein sour gasolines were sweetened by percolation in liquid phase at room temperature through beds of bauxite. In run No. 2, the bauxite treating agent had been prepared by saturating a fresh commercial granular ignited bauxite (containing about 15% iron compounds as Fe_2O_3) with gaseous ammonia and removing excess ammonia by heating the bauxite at 250–450° F. under an absolute pressure of about 1 mm. Hg for two hours. In run No. 4, the treating agent had been prepared according to the procedure of run No. 2 followed by saturating the bauxite with an about 60% solution of ferric chloride in water, washing with 20 cc. of distilled water, and then with a 28% (as NH_3) solution of ammonium hydroxide in water until the effluent liquid was free of precipitate, and removing excess water by heating at 250–400° F. and 1 mm. Hg for 3 hours. In run No. 6, the treating agent had been prepared by gently boiling for about 15 minutes a mixture of 130 cc. of a magnetically separated "high iron" bauxite containing 55% of iron compounds as Fe_2O_3 with 10 grams of sodium hydroxide and 200 cc. of water, washing the bauxite with water until the pH of the effluent was about 7, and heating at 300–400° F. and 1 mm. Hg for 3 hours.

Run No. 1 is a comparison run for run No. 2, the ammonia treatment having been omitted and the bauxite heated at 300–400° F. and 1 mm. Hg. Run No. 3 is a comparison run for run No. 4, the ammonia, ferric chloride, and ammonium hydroxide treatment having been omitted and the bauxite heated at 300–400° F. and 1 mm. Hg. Run No. 5 is a comparison run for run No. 6, the sodium hydroxide treatment having been omitted and the bauxite heated at 400–620° F. and 1 mm. Hg.

In some of the runs, as indicated in the following table, straight run gasoline was employed as charge stock and in others thermal gasoline. In some runs, as indicated in the table, the charge gasoline was dried by passing through calcium sulfate ("Drierite") prior to passing through the bauxite, and in other runs the charge gasoline was not dried.

In each run, separate samples of effluent gasoline from the bauxite bed were collected, the usual size of sample being 4000 cc. In each run, the amount of bauxite in the bed was 60 cc. or 64 cc. The various effluent samples were tested for mercaptan content by titrating with a standard aqueous solution containing copper ions. In each run, the amount of effluent collected before the percent mercaptan sulfur of the effluent substantially exceeded 0.0001 percent, was determined. This amount indicated the capacity of the bauxite for producing gasoline having mercaptan content not exceeding 0.0001 percent.

The following table shows the results obtained:

Run No.	Gasoline	Initial RSH, Percent	Bauxite	Capacity, cc.
1	Straight run, undried	0.0034	Ordinary, untreated	8,000
2	do	0.0030	Ordinary, NH_3 treated	16,000
3	Straight run, dried	0.0027	Ordinary, untreated	28,000
4	do	0.0020–0.0035	Ordinary, Fe and NH_3 treated	64,000
5	Thermal, undried	0.0012	High iron, untreated	16,000
6	do	0.0007–0.0010	High iron, NaOH treated	44,000

The superiority of run 3 to run 1 is probably attributable to the drying of the charge gasoline. In run No. 6, the mercaptan content of the gasoline charge was about 0.0010% for the first 20,000 cc. charged, about 0.0009% for the next 12,000 cc., and about 0.0007% for the next 12,000 cc. The superiority of run 6 to run 5 is clear, in spite of the somewhat lower initial mercaptan content in run 6.

In runs 1, 2, 3 and 6, the space rate was about 5 volumes of gasoline per volume of bauxite per hour throughout the run. In run 5, the space rate was 8 for the first 4000 cc. charged and 5.5 for the next 12,000 cc. charged. In run 4, the space rate was 9 for the first 52,000 cc. charged and 5 for the next 12,000 cc. charged. The mercaptan content of the effluent rose gradually to 0.0006% during the use of the 9 space rate and then dropped to an amount equal to or less than 0.0001% when the space rate was reduced to 5. When the run was terminated at 64,000 cc. of effluent, the mercaptan content of the last effluent sample did not exceed 0.0001%. This indicates that at space rate of 5, the bauxite of run 4 would have had a capacity of at least

64,000 cc., and therefore the figure of 64,000 cc. is reported in the table.

This example shows that ammonia or sodium hydroxide treatment of fresh bauxite containing iron compounds increases the ability of the bauxite to reduce the mercaptan content of straight run or thermal gasoline. Other experiments have shown that alkali-treated bauxite is also effective in reducing the mercaptan content of catalytically cracked gasoline. Thus, in a run (No. 7) generally similar to run 6 but employing catalytic gasoline as charge and a more severe alkali treatment (50 grams of sodium hydroxide and 150 cc. of water per 130 cc. of bauxite), a capacity of 24,000 cc. at space rate of 5 was obtained.

Example II

After 72,100 cc. of thermal gasoline had been percolated through the bauxite in run 6 of Example I, the mercaptan content of the effluent having risen to 0.0003–0.0004% by that time, the flow of gasoline was ceased, and steam was passed through the bauxite bed for 7 hours. The bauxite was then heated at 400–500° F. and 1 mm. Hg for 3 hours, followed by wetting with naphtha. Then the flow of thermal gasoline, this time having initial mercaptan content of 0.0011%, was resumed at space rate of 5. The space rate was lowered to 3 after 32,000 cc. of effluent had been collected. The capacity of the steam-regenerated bauxite was found to be 36,000 cc., i.e. that much of effluent was collected before the cercaptan content of the effluent substantially exceeded 0.0001 percent.

This example shows that a caustic-treated high iron bauxite (60 cc.) having 44,000 cc. capacity for thermal gasoline at space rate 5 can be regenerated with steam to produce a regenerated bauxite having 36,000 cc. capacity for thermal gasoline at an average space rate of approximately 5.

Example III

After 32,100 cc. of catalytic gasoline had been percolated through the bauxite in run 7 of Example I, the mercaptan content of the effluent having risen to 0.0003% by that time, the flow of gasoline was ceased, and steam was passed through the bauxite bed for one hour. Then 200 cc. of 10% caustic soda were percolated through the bed at room temperature. Following this, the bed was filled with 10% caustic soda and heated at steam temperature for one hour. Then the bed was drained and water washed at steam temperature until the pH of the effluent water was about 7. The bauxite was then heated at 460° F. and 1 mm. Hg for 3 hours. The flow of catalytic gasoline, now having initial mercaptan content of 0.0009–0.0010% was resumed. The capacity of the caustic-regenerated bauxite was found to be 12,000 cc.

This example shows that a caustic-treated high iron bauxite (60 cc.) having 24,000 cc. capacity for catalytic gasoline at space rate 5 can be regenerated with caustic to produce a regenerated bauxite having 12,000 cc. capacity for catalytic gasoline at space rate 5.

Bauxite is a preferred adsorbent for use according to the invention, but other adsorbents can also be suitably employed. Any of the well-known adsorbents for treatment of mineral oil fractions can be employed, e.g. fuller's earth, silica gel, Attapulgus clay, Filtrol clay, infusorial earth, etc. If the adsorbent employed does not initially contain substantial amounts of iron, for example 1% or more, iron should be added to the adsorbent prior to the ammonium treatment according to the invention. A particularly advantageous adsorbent is a magnetically separated bauxite containing about 10 to 70 weight percent, more preferably 30 to 60 weight percent, of iron compounds as Fe_2O_3. An adsorbent which is used according to the invention can be one which has been ignited or calcined prior to treatment with an alkali, or one which has not been ignited or calcined.

Temperatures ordinarily employed in igniting or calcining are those in the approximate range from 600° F. to 1400° F.

The process of the invention is particularly advantageously applied to gasoline fractions containing mercaptans, but other petroleum fractions can also be treated for reduction of mercaptan content, for example spirits, naphtha, kerosene, etc. Preferably, a petroleum fraction treated according to the invention has not been acid treated directly prior, or remotely prior, to the adsorbent treatment. Straight run or cracked petroleum fractions can be treated. However the yield of low-mercaptan products obtainable with straight run fractions is substantially greater than that obtainable with cracked fractions. It is believed that, in the case of cracked fractions, these materials contain constituents such as phenols, etc. which become adsorbed on the adsorbent and interfere with the reduction of mercaptan content.

The process of the invention involves in some embodiments contacting hydrocarbons with an adsorbent prepared by contacting a fresh iron-containing adsorbent with an alkali; a fresh adsorbent being one which has not previously been used to reduce the mercaptan content of hydrocarbon materials. Preferably, excess alkali is removed from the alkali-treated adsorbent prior to use of the latter to treat hydrocarbons. However, in some cases this may not be necessary.

In copending application Serial No. 480,296, filed January 6, 1955, by the present inventors, a method for reducing the mercaptan content of mineral oil is disclosed and claimed, such method comprising contacting mineral oil containing mercaptans in liquid phase with magnetically separated bauxite containing about 20 to 70 weight percent of iron compounds as Fe_2O_3.

The invention claimed is:

1. Process for reducing the mercaptan content of hydrocarbons which comprises contacting hydrocarbons containing mercaptans in liquid phase in the presence of oxygen with a porous solid adsorbent treating agent which has previously been exposed to temperature not exceeding 1400° F., said treating agent having been prepared by contacting a porous solid adsorbent material containing iron compounds with an alkali and removing excess alkali and any excess moisture from the adsorbent by procedure comprising heating to a temperature above the volatilization temperature of water under the prevailing conditions but not substantially above 600° F., said treating agent containing combined water remaining after said heating.

2. Process according to claim 1 wherein said adsorbent is bauxite.

3. Process according to claim 2 wherein said adsorbent is magnetically separated bauxite containing about 10 to 70 weight percent of iron as F_2O_3.

4. Process according to claim 1 wherein said alkali is an alkali metal hydroxide.

5. Process according to claim 4 wherein said removing is accomplished by washing the adsorbent with water until the pH of the effluent water is below 8.

6. Process according to claim 1 wherein the alkali is aqueous sodium hydroxide.

7. Process according to claim 6 wherein the amount of alkali employed is about 0.5 to 2 moles of alkali per mole of alumina in the bauxite.

8. Process according to claim 1 wherein said alkali is ammonia.

9. Process according to claim 1 wherein the adsorbent has been contacted with an aqueous solution of an iron compound prior to contacting with alkali.

10. Process according to claim 1 wherein the first-named contacting is effected at approximately atmospheric temperature.

11. Process according to claim 1 wherein said treating agent is prepared by saturating fresh granular bauxite

with aqueous ferric chloride of at least 10 weight percent concentration, then contacting the bauxite with aqueous ammonium hydroxide until the aqueous effluent is free of precipitate, and removing excess water from the bauxite.

12. Process according to claim 1 wherein said removing is effected by heating the adsorbent to a temperature in the approximate range from 150° F. to 600° F. at an absolute pressure less than about 100 mm. Hg.

13. Process according to claim 1 wherein said hydrocarbons are straight run gasoline.

14. Process according to claim 1 wherein said hydrocarbons are cracked gasoline.

15. Process according to claim 1 wherein said treating agent contains 1 to 25 weight percent of iron.

References Cited in the file of this patent

UNITED STATES PATENTS

962,841	Hood et al.	June 28, 1910
1,098,764	Richter	June 2, 1914
1,687,992	Phillips et al.	Oct. 16, 1928
1,957,794	Morrell et al.	May 8, 1934
2,042,053	Hoover	May 26, 1936
2,154,424	Dolbear	Apr. 18, 1939
2,250,915	Kolthoff et al.	July 29, 1941
2,322,674	Thomas	June 22, 1943
2,326,369	La Lande	Aug. 10, 1943
2,377,546	Frey	June 5, 1945
2,422,875	Agren	June 24, 1947