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DESULFURIZING ADSORBENT AND PROCESS FOR PREPARING SAME

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This invention relates to a new product and process of producing the same, useful in the catalytic purification, desulfurization, and conversion of hydrocarbon gases and liquids. It is primarily concerned with a novel catalytic mass containing as essential elements an aluminous carrier material and a finely divided activated metallic compound carried thereby. More specifically, the invention contemplates the preparation of a new hard stable granular activated product containing a mixture of iron oxide and fuller's earth of the Georgia-Florida type, and the novel product resulting therefrom.

In the prior art the removal of sulfur present as hydrogen sulfide from gases has been practiced by the so-called dry box purification process, which utilizes finely powdered iron oxide deposited on wood shavings, the combination being known to the art as iron oxide "sponge." A number of disadvantages attendant upon this prior art process are that the sponge is bulky and requires the use of large volumes of the same; regeneration of the sponge must be accomplished by removing the exhausted sponge from the box and to prevent burning of the same by appropriate wettings; regeneration of the wood shavings sponge can only be accomplished a few times as the sponge builds up a quantity of deposited sulfur which cannot be removed. The chemistry of the removal of hydrogen sulfide has usually been indicated as follows:

$$Fe_2O_3+3H_2S\rightarrow Fe_2S_3+3H_2O+heat$$

Oxygen which may also be present in the gas causes hydrogen sulfide to be removed with deposition of sulfur as follows:

$$2H_2S+O_2\rightarrow 2H_2O+2S+heat$$

When this sponge material of the prior art is revivified, the following reaction takes place:

$$2Fe_2S_3+3O_2\rightarrow 2Fe_2O_3+6S+heat$$

All of these difficulties are avoided and solved by the present invention, wherein a relatively small amount of catalytic mass replaces the bulky sponge of large volume; which permits many regenerations of the mass without discarding the same; and which permits the entire mass to be regenerated in place in the vessel in which it is used, without the trouble of emptying the same; and which permits the removal of all the sulfur formed during revivification, so that sulfur built up is substantially eliminated.

The present invention utilizes fuller's earth as

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the carrier or support for activated iron oxide, and thus allows the use of a wide variety of conditions for regeneration and use. In accordance with the present process, the transfer of sulfur in the form of hydrogen sulfide from the gas or liquid to be purified is accomplished by reactions similar to the above, as in the old iron sponge process, but the revivified mass of material is cleared of sulfur at a high temperature and by the use of steam whereby the sulfur is burned to SO_2 at a temperature above 500° F. and whereby iron sulfide is oxidized or regenerated back to iron oxide by air and steam. The specific reactions during regeneration are as follows. With the presence of steam only the following takes place:

$$Fe_2S_3+3H_2O+heat\rightarrow 3H_2S+Fe_2O_3$$

The catalytic mass can be virtually completely regenerated according to the aforesaid reaction, but the reaction takes place slowly as the regeneration approaches completion. However, with the introduction of air or any oxygen containing gas, the following exothermic reaction occurs in addition to the aforesaid reaction, allowing the regeneration to be completed in an appreciably shorter time:

$$2Fe_2S_3+3O_2\rightarrow 2Fe_2O_3+6S+heat$$

and at the temperatures of 500° F. and over, this takes place:

$$S+O_2\rightarrow SO_2+heat$$

The liberation of heat is beneficial to the regeneration as it vaporizes any sulfur not eliminated as gaseous SO_2 and sweeps out any oily, cracked or polymerized products from the gas being treated.

A further feature of the invention is the removal of mercaptans (thiols) from gases, liquids, and petroleum distillates. This is of particular significance, since the old dry box purification process cannot be used for removal of mercaptans from liquids or petroleum distillates. The catalytic mass of the present invention may be applied to petroleum distillates containing other sulfur containing compounds, such as

Thiophanes	Thio-aldehydes
Thiophene	Thio-ketones
Polysulfides	Penthiophene
Sulfonic acids	Thionaphthene
Sulfoxides	Diphenylene sulfide
Sulfones	Thianthrene

As an example of the preparation of the catalytic material of the present invention, iron oxide

is thoroughly mixed with fuller's earth containing a sufficient amount of its natural water of hydration to preserve its gelling properties. A third ingredient, the purpose being to supply alkalinity to the mix, such as sodium carbonate, may be added to the mixture. Water is then added to give plasticity to the mass, and the whole is pugged, then extruded or pelleted to form shapes, which can be dried, activated and transported by conventional equipment. A wide range of temperatures may be used for drying and activating the mixture, depending upon the service to which it is to be put. This may range from 230° to 1400° F. to constant weight at these temperatures. However, when the mixture is to be used for treatment of aqueous mediums or wherever water may come in contact with the mass, temperatures of 700° to 900° F., or higher, should be used for activation. When subjected to temperatures of this order, fuller's earth becomes resistant to water and loses its power to gel or form a mud. Further, it has a binding action on the iron oxide, forming a hard body with the oxide, which can be ground and meshed to give a granular product of good mechanical strength, chemical activity and adsorption capacity.

Such a composition of material will selectively adsorb hydrogen sulfide from gases and will adsorb hydrogen sulfide and mercaptan sulfur from liquids, or by a different method of use will convert hydrogen sulfide and mercaptan sulfur in liquids to a form that for most purposes is much less objectionable. It can be regenerated in place with the use of steam and air to a high degree of capacity and efficiency.

Examples of the invention are as follows:

EXAMPLE 1

291 grams of air dried Georgia-Florida fuller's earth, finely ground, was intimately mixed dry with 872 grams of iron oxide having the following analysis:

	Per cent
Moisture at 105° C	8.02
Fe_2O_3	72.86
Al_2O_3	2.10
TiO_2	None
Na_2O	3.48
Volatile above 105° C	13.54

To this was added 430 ml. of distilled water and the whole mass kneaded together and extruded. The extruded rods resulting were then air dried on the floor, grounded to a $^{16}/_{20}$ mesh particle size, activated to equilibrium weight at 1000° F. The activated granules were then weighed into a U-tube and hydrogen sulfide gas introduced. The test was discontinued when the exit gas discolored lead acetate paper, at which time the mixture was found to have adsorbed 3.9% of its weight in hydrogen sulfide.

EXAMPLE 2

568 grams of finely ground, air dried Georgia-Florida fuller's earth was intimately mixed dry with 1704 grams of activated iron oxide of the analysis of Example 1. The mass was then kneaded with water and extruded. After air drying, it was ground and screened to $^{8}/_{16}$ mesh and activated at 800° F. for one hour. 195 grams of the activated mixture was charged to a straight glass 2.6 cm. diameter tube to give a 42 cm. column on top of a wire supporting screen. Hydrogen sulfide gas was then introduced. The exit was tested for hydrogen sulfide with lead acetate paper. The test was discontinued when the paper became discolored, at which time the adsorbent had taken up 33.2% of its weight in hydrogen sulfide. The adsorbent was saturated with hydrogen sulfide and regenerated in place four times by the use of steam and air. The capacity after the fourth regeneration was 24.7%. Regeneration was carried out as follows:

1. After the hydrogen sulfide stream was shut off, superheated steam was introduced into the column.

2. When the column temperature had reached a constant value, as evidenced by the temperature of the exit steam, air was introduced into the bed, along with the continued introduction of steam. This caused a rapid rise in temperature and greatly increased the effectiveness of the regeneration by elimination of sulfur as sulfur dioxide, as well as hydrogen sulfide and elemental sulfur. After cooling down, it was ready for reuse. A typical time-temperature record of the exit regenerating gas is as follows:

TABLE I

Regeneration Time, Minutes	Exit Temperature
STEAM ONLY	
	°F.
0	208
13	208
40	384
46	430
59	484
81	484
AIR INTRODUCED	
95	494
98	530
101	604
108	628
116	645
119	663
123	650
133	564
141	548
175	400

EXAMPLE 3

A 15 inch column (140 grams) of $^{30}/_{60}$ mesh iron oxide-Floridin mixture, activated at 900° F. was placed in a glass tube and a naphtha solution of mercaptan sulfur solution containing .00254 gram per 25 ml. was percolated through at a rate of one ml. per minute. 10,500 ml. of mercaptan solution was passed through the column before any mercaptan was detectable in the exit naphtha. This corresponds to a yield of 18,000 gallons per ton and a capacity for mercaptan sulfur of 1.5%. The introduction of naphtha was continued although the efficiency of mercaptan removal decreased, but at 11,700 ml. (20,000 gallons per ton) through-put, the adsorbent was still removing 72% of the mercaptan sulfur entering.

EXAMPLE 4

A raw gasoline having an initial boiling point of 98° F. and an end point of 388° F., which was sour to the Doctor test and which contained .033% sulfur, was percolated at a rate of 3 ml. per minute through a 15 inch column of $^{30}/_{60}$ mesh fuller's earth-iron oxide mixture, activated at 1200° F., and having a composition of 80% by weight of iron oxide. At a yield of 19,050 ml. (32,743 gallons per ton), 58.2% of the mercaptan sulfur entering had been removed and the composite yield was sweet to the Doctor test.

EXAMPLE 5

A test unit tower was charged with 11 pounds of 4/16 mesh fuller's earth iron oxide mixture, activated at 1200° F. and a natural gas containing 30 grains of sulfur per 100 cubic feet at a maximum pressure of 36 pounds per square inch was passed therethrough. After two hours' run hydrogen sulfide was detected with lead acetate. The gas was allowed to continue flowing overnight, regeneration being carried out the next morning. Superheated steam was admitted to the test unit tower, raising the temperature to 500° F. The introduction of air and steam into the tower caused a rise abruptly from 500° to 640° F. It was then allowed to stand overnight to cool. The next day a test run at a flow rate of 120 cubic feet per hour (25 feet per minute) produced gas that was sweet to lead acetate for approximately eight hours.

EXAMPLE 6

A naphtha containing various types of sulfur compounds was distilled in an apparatus so arranged that the naphtha vapors passed through a heated column containing 220 grams of 16/30 mesh iron oxide-Floridin mixture, activated at 1000° F. and were then condensed and collected. In one test, the heated column was held at a temperature of 400° F.; in another test, the heated column was held at a temperature of 500° F. In both tests, all sulfur present as hydrogen sulfide and mercaptan sulfur was completely removed and the total sulfur content of the naphtha was substantially reduced. These results are summarized in Table II.

TABLE II

Removal of sulfur from naphtha in the vapor phase

Sulfur present in the form of—	Original untreated naphtha	Naphtha treated with iron oxide Floridin mixture at 400° F.	Naphtha treated with iron oxide Floridin mixture at 500° F.
	Per cent	*Per cent*	*Per cent*
Hydrogen sulfide	.0038	.0000	.0000
Mercaptan sulfur	.0560	.0000	.0000
Elementary sulfur	.0000	Trace	.0005
Disulfides	.0157	.0031	.0038
Sulfides	.0159	.0221	.0225
Residual sulfur	.0221	.0181	.0175
Total sulfur	.1135	.0433	.0443

From all the above tests it will be seen that the adsorption capacity of the catalytic product is approximately up to 7% of its weight for hydrogen sulfide, and its adsorption efficiency is practically up to 100%, up to its full capacity. When made into an adsorbent bed, after the bed has become exhausted for adsorption of H_2S, the gas flow should be cut off and steam used to flush out all the remaining vapors. The bed is then heated up to 450–500° F. After the temperature of the bed reaches a steady state, a small quantity of air is introduced cautiously and simultaneously with the steam, the temperature of the bed being controlled by the introduction of the air so that it does not exceed 700° F. After the reaction is completed, the temperature returns rapidly to that of the introduced steam, at which point the introduction of air is discontinued and the steam is continued until all of the air has been flushed out of the bed. The bed may then be cooled by one or a combination of the following:

A. Cooling coils.
B. Inert gas such as nitrogen or CO_2.
C. Introduction of cold, sweet gas.
D. Natural cooling, such as standing overnight.

While fuller's earth of the Georgia-Florida type is the preferred carrier, other types of fuller's earth may be used. Iron oxide is the preferred metallic oxide, but the invention is not restricted thereto. Zinc oxide, copper oxide, and nickel oxide may be used singly or in combination, or else in conjunction with iron oxide. The dry box container may be replaced with other suitable containing means. The extrusion step referred to may be such as is carried out in accordance with the description of the Hartshorne Patent No. 2,079,854, May 11, 1937, although the invention is not slavishly restricted to an extrusion step. The use of Raschig rings prepared from the new catalytic material is contemplated. In the conversion of hydrocarbons, whereby gasoline is produced by a liquid or vapor phase cracking process, the new catalytic material may be employed.

The fuller's earth and iron oxide may be mixed in any proportions; the preferred proportions range from 70–90% iron oxide by weight. An agent to confer alkalinity on the catalytic mass may be an essential part of the originally used iron oxide or it may be added to the mixture before or after activation thereof. Sodium carbonate is preferred to confer alkalinity, but other alkalies or basic substances may be utilized without departing from the spirit and scope of the invention.

Although we prefer to use fuller's earth of the Georgia-Florida type, such as has been generally known by the name "Floridin" for many years, it will be understood that we may use any fuller's earth or similar material that can be made into hard granules and to which the iron oxide or other ingredient can be firmly bonded as herein disclosed to give a suitable adsorbent.

While air is the most practical oxygen-containing gas to use in regeneration, cylinders of compressed oxygen may be economically purchased and used. Flue gases could also be used, although their oxygen content would be rather low.

We claim:

1. The method of preparing a new desulfurizing adsorbent which consists solely of fuller's earth and iron oxide, the iron oxide being in greater amount than the fuller's earth and in amount of 70 to 90% by weight, said method consisting in mixing the fuller's earth containing a sufficient amount of its natural water of hydration to preserve its gelling properties with iron oxide, plasticizing the mixture, extruding the mass, and heating the extruded mass at a temperature from 230° F. to 1400° F. to activate the same.

2. The method in accordance with claim 1 in which the mixture is rendered alkaline.

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