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PROCESS OF DESULFURIZATION EMPLOYING ALKALI AND NITROGEN DIOXIDE

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This invention relates to new and useful improvements in processes for the refining of light petroleum distillates which contain a substantial quantity of malodorous sulfur compounds. More particularly, this invention is concerned with a process for deodorizing and desulfurizing light petroleum distillates by treatment with nitrogen dioxide at about 0°–35° C., followed by successive washing with aqueous caustic and water.

Petroleum fractions, e.g., naphthas, kerosines, gasolines, fuel oil, lubricating oil, waxes, etc., as normally obtained from petroleum often have unsatisfactory odor characteristics resulting from the presence of malodorous sulfur compounds of various types. The removal of these malodorous constituents has often proved difficult by ordinary refining procedures. In the past, the removal of mercaptans has been accomplished to some extent by clay treating and by treatment with chemicals which form readily extractable derivatives. In some cases, the removal of sulfur compounds has been impractical and the sour petroleum fractions have been treated by a sweetening process in which mercaptans are converted to disulfides (which have less objectionable odors). A process of this type, however, does not remove sulfur from the product and may result in a product which is undesirable even though free of odor of mercaptans.

In the past, petroleum fractions have been treated with a variety of chemicals for producing products with substantially improved odors. Naphthas have been treated with adsorbents of various types, and have been treated with various amines during distillation to prevent formation of malodorous constituents. Petroleum fractions have been subjected to solvent extraction with various acidic materials such as sulfur dioxide, phenol, and concentrated acids to extract color-forming and odor-forming constituents. The processes of the prior art, however, have been expensive and difficult to carry out and have not always produced products of good odor characteristics which are free of sulfur compounds.

It is therefore one object of this invention to provide a process for the treatment of light petroleum distillates which results in the elimination of mercaptans, reduction in content of other sulfur compounds, and a substantial improvement of odor.

A feature of this invention is the provision of a process for the treatment of light petroleum distillates with nitrogen dioxide at about 0°–35° C., followed by washing of the treated distillate with aqueous caustic and water.

Other objects and features of this invention will become apparent from time to time throughout the specification and claims as hereinafter related.

In measuring the relative odor of petroleum products it has not been possible to develop a precise, quantitative measure of odor which is entirely independent of the individual who evaluates the odor. Nevertheless, there are certain procedures for rating odors which have been used in the petroleum industry. Odor evaluation standards and methods have been proposed by a joint committee of the ASTM and TAPPI. A modification of this procedure has been used extensively in the evaluation of the odor of commercial petroleum products. In a typical petroleum company, an odor panel is selected consisting of several, e.g., 10 to 20 or more, individuals who have

been tested for their ability to discriminate between and match different odors. One test for selection of panel members involves correctly matching a series of chemical odors such as very dilute odors of acetic acid, phenol, toluene, and benzene. A second test involves a matching of a variety of different naphthas by odor from a single manufacturing source. A third test involves the matching of mineral spirits obtained from different manufacturers. By use of these screening tests it is possible to select a panel of 10 to 20 individuals who are especially discriminating in evaluating odors of petroleum products. In the rating of odors of petroleum fractions such as an odorless naphtha, a numerical rating scale has been established to describe odor quality.

Numerical rating:	Odor quality
1	Excellent.
2	Excellent.
3	Very good.
4	Very good.
5	Good.
6	Fair (just passing).
7	Borderline.
8	Borderline.
9	Poor.
10	Very poor.

When evaluating the odor of petroleum naphthas the following procedure is used. The members of the odor panel are requested to avoid contact with contaminating odors, e.g., smoking, etc., for at least ½ hour prior to the test. The odor evaluation is carried out in an air-conditioned room, at about 24° C., which is as free as possible from extraneous odors. Each member of the test panel rates the odor of a product separately. A non-member of a panel conducts the test and is present to record any pertinent comments made regarding the odor. To eliminate bias, the product samples are coded, and the panel members are told the type of product being rated. To avoid odor fatigue, no more than three samples are rated at any one time. Any additional ratings are spaced by at least three hours. A total of seven panel members rate the product and the average of these opinions is reported as the odor rating.

In preparing the naphtha for odor evaluation, a 35-ml. representative portion is poured into a clean, odor-free, eight-ounce French square bottle. The bottle is sealed with a clean, odor-free, screw-on cap. The same sample is used by all members of the panel. The type bottle used in the evaluation is the same as that used in the screening tests for selection of the panel member. The panel member evaluates the odor of the naphtha by removing the cap from the bottle, placing his nose at the bottle mouth and sniffing the odor. He checks the intensity of odor and for any foreign or undesirable odor that may be present, and then numerically rates the odor using the above-described scale. This method is called the "wet-odor" of the naphtha.

Sulfur compounds, such as mercaptans, sulfides, and disulfides, are often present in petroleum fractions. In many cases, it is necessary to remove a substantial portion of the sulfur compounds in order to produce petroleum products of high quality. We have devised a process for the reduction of sulfur content and improvement in color and odor of light petroleum distillates. Our process consists essentially of the following steps: (1) A sour light petroleum distillate is treated with gaseous nitrogen dioxide at a low temperature in the range from about 0°–35° C. The nitrogen dioxide may be charged alone or in admixture with inert gaseous diluents such as nitrogen, hydrogen, helium, etc. In general, the amount of

nitrogen dioxide should be at least equal to the stoichiometric amount required to react with all of the sulfur compounds in the petroleum distillate being treated. However, because the amounts of each of the types of sulfur compound present are difficult to determine, and because all of the reactions which occur in this process have not been determined, the amount of nitrogen dioxide required is best determined by a screening test treatment of a small sample of the distillate. The product from the first step may be yellow in color. (2) The treated petroleum fraction is washed with aqueous caustic until all of the yellow color has been removed. (3) The product is finally washed with water until all alkaline material has been removed, and the product may be dried if necessary.

In carrying out this invention we have found that all three steps of our process are essential to obtaining a mercaptan-free, colorless product of diminished sulfur content and improved odor. When any of the above-noted steps of treatment are eliminated, an unsatisfactory product is obtained. When the product is treated with nitrogen dioxide and washed only with water, the product tends to have an unsatisfactory yellow color. When the treatment with nitrogen dioxide is omitted, the yellow color does not occur but there is no appreciable reduction in odor or sulfur content, whether washed with water or caustic. When the temperature of the NO_2 treatment exceeds 35° C., there is an undesirable oxidation of hydrocarbon constituents which may produce additional malodorous compounds. The mechanism by which the process operates to sweeten and reduce the sulfur content of light distillates is not known precisely. The treatment probably involves the conversion of mercaptans to disulfides, and the conversion of disulfides and monosulfides to sulfoxides or sulfones, or to unknown derivatives which are somehow rendered soluble by treatment with aqueous caustic. Whatever the identity of the reaction products and the mechanism of the reactions, the net result is that the sulfur compounds are converted to products which can be readily separated from the petroleum fraction by washing with water and aqueous caustic. We have no explanation for the yellow color produced by the nitrogen dioxide treatment. The material which causes this color is not water-soluble and the material which produces the color is unknown in composition. The removal of the color by caustic washing may be due to solubility of the colored material in aqueous caustic or the colored material may be converted by the caustic to a water-soluble material which is removed.

The following non-limiting examples are illustrative of the scope of this invention.

Example I

A light petroleum distillate (a naphtha) having the distillation range: I.B.P. 44° C., 5% 58° C., 50% 127° C., 95% 200° C., and E.P. 212° C., was treated partially in accordance with this invention. This naphtha was evaluated sour by the doctor test and had an odor rating of 9. It had a total sulfur content of 0.087% wt., most of which consisted of mercaptans, sulfides, and disulfides. In this experiment a 500-ml. 3-necked flask was fitted with a fritted gas bubbler, a stirrer, a thermometer, and a condenser. The flask was cooled with an ice-water bath and charged with 300 ml. of the sour naphtha. Nitrogen at 30 cc./min. and gaseous nitrogen dioxide at 179 cc./min. were bubbled through the naphtha for 30 minutes, with stirring. A total of 10.1 g. of nitrogen dioxide was charged. Next, the naphtha was placed in a 500-cc. separatory funnel and washed six times with 200 ml. portions of water. The final water wash was neutral as measured by pH paper. The naphtha was dried by filtering it through a double thickness of filter paper. The final product was doctor sweet, had a total sulfur content of 0.021% wt., and had a fairly pleasant odor (odor No. about 3), but was bright yellow in color.

Example II

In another experiment, a fresh 300-ml. batch of the sour naphtha used in Example I was charged to the apparatus described in Example I. In this experiment, nitrogen was bubbled through the naphtha at 60 cc./min. for 30 minutes, with stirring, without any nitrogen dioxide being added. Then the naphtha was washed six times with water and filtered through a drying paper (Reeve Angel paper). The product which was obtained in this experiment was colorless but was definitely sour, had an odor rating of about 7–8, and a sulfur content of about 0.083% wt.

Example III

In another experiment, a fresh 300-ml. batch of the sour naphtha used in Examples I and II was charged to the apparatus described above. Nitrogen at 30 cc./min. and gaseous nitrogen dioxide at 53 cc./min. were bubbled through the naphtha for 10 minutes, with stirring. At this point, a slight yellow-brown color began to appear above the liquid. A total of 1.0 g. of nitrogen dioxide was charged. The treated naphtha was then washed five times with water and the final wash was neutral to pH paper. The treated naphtha was filtered and stored overnight. The color of the product was a clear, bright yellow. The next day the odor of the naphtha was found to be slightly acidic and characteristic of the oxides of nitrogen. The treated naphtha was then washed with four 50-ml. batches of 0.4 N sodium hydroxide. This treatment removed both the color and the acidic odor. Finally, the naphtha was washed four times with water and dried by filtering as before. The product was doctor sweet, had an odor No. of 2, and was reduced about 50% in total sulfur content, substantially all of the mercaptans having disappeared from the product.

Example IV

In still another experiment, a fresh 300-ml. batch of the original sour naphtha was washed with four 50-ml. batches of 0.4 N sodium hydroxide without receiving the nitrogen dioxide treatment. The product was then washed four times with water and dried by filtering. The product was strongly doctor sour, although the odor was slightly improved over the original naphtha.

From our experiments we have found that this treatment is applicable broadly to light petroleum distillates only, i.e. distillates boiling in the range from 38° to 288° C. When a petroleum distillate boiling in this range is treated with nitrogen dioxide, with or without a diluent gas, the sulfur compounds are converted to a form which can be extracted with aqueous alkali. The nitrogen dioxide must be added in an amount not less than the stoichiometric amount required to react with all of the sulfur compounds in the distillate, preferably 1 to 10 g. nitrogen dioxide per gram of sulfur in the material being treated. The treatment with nitrogen dioxide must be carried out at relatively low temperatures, preferably in the range of 0° to 35° C., since the use of higher temperatures causes the nitrogen dioxide to attack some of the hydrocarbons in the distillate. The treatment is carried out for a time sufficient to effect complete reaction with the sulfur compounds, preferably in the range of 5 to 30 minutes. The light distillate which has been treated with nitrogen dioxide is washed with aqueous alkali, preferably 0.1 to 2.0 N sodium hydroxide, although other alkali such as potassium hydroxide, lithium hydroxide, or ammonium hydroxide may be used. The final wash with water is carried out for a time sufficient to render the product free from alkali.

The combination of steps used in this process are effective to remove substantially all of the mercaptans from the distillate, as well as a major portion of other sulfur compounds, while the treatment with alkali removes the undesirable color-forming materials which are produced during the nitrogen dioxide treatment. While

the treatment has been described specifically as applied to a sour naphtha, it is applicable to other distillates boiling in the range of 38° to 288° C., including gasolines, light naphthas, medium naphthas, kerosine, and light hydrocarbons, such as heptane, benzene, toluene, etc., which contain malodorous sulfur compounds. In each case, the treatment is effective to remove substantially all of the mercaptans as well as a major portion of other sulfur compounds, while rendering the product doctor sweet. The product which is finally recovered from the process is not only doctor sweet, but is improved in odor from an initial rating in the range of about 9–10 to a rating in the range of about 1–3.

While we have described our invention fully and completely with special emphasis upon several preferred embodiments, we wish it to be understood that within the scope of the appended claims this invention may be practiced otherwise than as specifically described herein.

The embodiments of the invention in which an exclusive property or privilege is claimed are as follows:

1. A method of producing petroleum products of diminished sulfur content and improved odor which consists essentially of contacting a sour light naphtha with nitrogen dioxide at about 0°–35° C., washing the treated distillate with aqueous alkali until free of color, and washing the color-free product with water until free of alkali.

2. A method in accordance with claim **1** in which the nitrogen dioxide is used in an amount not less than the stoichiometric amount required to react with all of the sulfur compounds in the naphtha.

3. A method of deodorizing and desulfurizing light naphthas which consists essentially of contacting a sour light naphtha with sufficient gaseous nitrogen dioxide, at about 0°–35° C., to react with substantially all of the sulfur compounds in the naphtha, washing the treated naphtha with a 0.4 N solution of NaOH in water until free of color, and washing the color-free product until neutral.

4. A method in accordance with claim **3** in which the naphtha is dried after the final washing.

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