United States Patent Office 2,882,232 Patented Apr. 14, 1959

2,882,232

IMPROVING THE ODOR OF SPECIALTY NAPHTHAS

Robert M. Haines and John W. Walsh, Crystal Lake, and Weldon G. Annable, Mundelein, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

No Drawing. Application November 14, 1955 Serial No. 546,785

8 Claims. (Cl. 252—50)

This invention relates to specialty naphthas. It is more specifically concerned with improving the odor characteristics of petroleum-derived industrial naphthas.

The re-odorizing of various substances by adding odor to them to disguise or conceal any disagreeable odors that may be an inherent characteristic is an old art. Products which are handled directly by the consumer are subject to his physiological reactions and, in spite of the service in which the material is consumed, they are subject to acceptance based upon their aesthetic appeal. Accordingly, it is necessary that products which have disagreeable properties, especially odor, be modified to transform the disagreeable odor to a pleasant one. In the case of unsatisfactory or undesirable odors this objective is effectuated by the use of odor masking agents or re-ordorants. The technique of re-odorizing is practical in many products, including a variety of petroleum products. One class of petroleum products which in recent years has achieved commercial significance is the highly refined naphthas. These goods are defined as selected fractions of the lighter, more volatile constituents of crude petroleum, chemically refined and separated into various boiling ranges. Although this definition includes aromatic compounds the instant invention is concerned only with straight-run or virgin products. Because of their good solvent properties, essentially nontoxic character, low corrosion, ready availability, and their functional versatility, petroleum naphthas can be prepared which are adaptable to a wide variety of industrial uses. It is therefore desirable that any odor which may be unpleasant or disagreeable to the consumer be changed. In some instances, petroleum products develop a rancid odor after an initial induction period. Generally, this type of odor is due to the oxidation of the hydrocarbons contained in the petroleum product and can be obviated by the use of additives which function as oxidation inhibitors. However, specialty naphthas have strong lacrymal and/or rhinitic effects which become in certain products more disagreeable when the naphtha is used in relatively high temperature processing. Although many qualitative and quantitative tests have been devised to control the properties of naphthas and insure their uniform quality, no standard test has been developed which will permit the evaluation of the odoriferous properties of naphthas. Petroleum naphthas may have a wet odor which occurs in naphtha in bulk form. They also may have a dry or residual odor which could be present in fabrics which have been in contact with petroleum naphthas, such as in the dry cleaning industries. Even though the dry cleaning solvent is substantially completely extracted from the goods being cleaned, there may persist in the goods an unpleasant odor attributed to the dry cleaning solvent.

In evaluating the odor characteristics of a petroleum naphtha, it is necessary to employ organoleptic panel testing for detecting the presence of off-quality odors in petroleum products. Although this test is entirely subjective, the qualitative and quantitative evaluation of odor is generally not susceptible to other analytical procedures.

This type of testing is used extensively in the evaluation of odor and flavor in foods and beverages. In general, the technique involves the selection of a carefully selected panel of several individuals which minimizes errors which might arise from the use of a single evaluation. Panel testing as a means for detecting odors is a recognized expedient for the determination of the type and source of odor and the level. For a more comprehensive discussion of the techniques of organoleptic panel testing, reference is made to Analytical Chemistry 24 (3), March 1952, at page 503; Modern Packaging 25 (11), July 1952, at page 145, and 26 (10), June 1953, at page 149.

It is therefore an object of this invention to re-odorize specialty petroleum naphthas. It is another objective of this invention to provide a petroleum naphtha free from lacrymal and/or rhinitic effects. Still another objective of this invention is to improve the odor of specialty naphthas. It is also an objective of this invention to improve the wet and/or dry or residual odors of specialty petroleum naphthas. These and other objectives will be apparent from the following detailed description of this invention.

According to this invention, improvement in the odor of specialty naphthas is provided by the addition thereto of trace amounts of an organic nitrile compound. It has been found that if small amounts of an organic nitrile, having not more than 12 carbon atoms per molecule, are admixed with a specialty petroleum naphtha, a composition free from irritating odors can be produced. The organic nitriles which can be employed in carrying out this invention include aliphatic and alicyclic nitriles, aromatic nitriles and alkaryl nitriles. Specific examples include but are not limited to acetonitrile, butyronitrile, caprylonitrile, isovaleronitrile, trideconitrile, benzonitrile, O-methylbenzonitrile, O-tolunitrile, napthylnitrile, cyclohexylbenzonitrile, cyclohexylnitrile, phenylbutyronitrile, phenylacetonitrile, etc. These additives have an inherent peculiar odor. However, when they are incorporated in a specialty petroleum naphtha possessing irritating odors, the blended composition has a substantially improved, mild odor having non-irritating characteristics. An important feature of the instant invention is the use of only trace amounts of the nitrile reodorant to bring about the objectives of this invention. While the exact amount of nitrile used will depend upon the naphtha boiling range, the source of the naphtha, the composition of the naphtha, the treatment of the naphtha, and the temperature at which the naphtha is to be used, it has been found that between 1–90 p.p.m. will provide satisfactory results, and in most instances about 10 parts per million will provide a specialty naphtha having a suitable odor. If more than about 90 parts per million are employed, there will be imparted to the naphtha composition an offensive nitrile odor which is as disagreeable as the strong, irritating odor normally present in the specialty naphtha. Although the wet and/or dry or residual odor of petroleum specialty naphthas is substantially improved by the addition of nitrile reodorants of this invention, the use of the more volatile nitriles is preferred when the wet odor is to be corrected, and less volatile nitriles are preferred for improving the dry or residual odor.

The petroleum specialty naphthas which can be reodorized according to this invention are low sulfur content, straight-run, specialty naphthas. These naphthas are produced from crude petroleum oils of the paraffinic, naphthenic or mixed base types, such as Pennsylvania, California, or Mid-Continent crude oils. These naphthas have boiling ranges between about 100° to 425° F., and have been refined by conventional refining processes to remove or convert the sulfur compounds contained therein to produce naphthas having a low sulfur content, as determined by the doctor test or distillation-corrosion

test. These tests are described by Henderson et al., in an article entitled "Effect of Sulfur and Sulfur Compounds in Naphtha Upon Certain Corrosion Tests," I. & E. Chemistry, Analytical Edition 12 (1), 1. Refined, straight-run petroleum naphthas, which pass the doctor test and the distillation-corrosion test and are low in sulfur content, containing not more than about 0.05% by weight of sulfur, are employed in this invention.

To illustrate the subject invention, a specialty petroleum naphtha, produced from a Mid-Continent-type crude petroleum oil and treated in a conventional Linde sweetening process, had the following characteristics:

Gravity	46.5° API.
ASTM boiling range, ° F.:	
I.B.P.	365° F.
50%	370° F.
E.P.	405° F.
Color	29.
Doctor test	Negative.
Distillation-corrosion test	Negative.
T.C.C. flash point	142° F.
H_2SO_4 absorption	1.5%.
Odor (panel testing)	Strong, irritating.

To this specialty naphtha was added 50 parts per million of caprylonitrile. In subjecting this to an organoleptic panel testing evaluation, it was found that a substantial improvement in odor was effected and the resultant composition had a mild and pleasant, non-irritating odor.

The foregoing example is an illustrative and non-limiting embodiment of this invention. The unusualness of this invention is made manifest by the use of selected organic nitriles which have disagreeable odors, per se, as reodorants for light petroleum distillates boiling in the naphtha range.

Therefore, we claim as our invention:

1. The method of preparing a specialty naphtha of satisfactory odor from refined straight-run petroleum naphtha of disagreeable odor, having a sulfur content sufficiently low to pass the "doctor test" and "distillation-corrosion test," which consists in blending with said naphtha at ambient temperature between 1 and 90 parts per million of an organic nitrile having not more than 12 carbon atoms per molecule, the amount of nitrile being sufficient to improve the disagreeable and unpleasant odor of said naphtha.

2. Method in accordance with claim 1 in which the nitrile is an aliphatic nitrile.

3. Method in accordance with claim 1 in which the nitrile is an alicyclic nitrile.

4. Method in accordance wit hclaim 1 in which the nitrile is an aromatic nitrile.

5. Method in accordance with claim 1 in which the nitrile is an alkaryl nitrile.

6. Method in accordance with claim 1 in which the nitrile is a caprylonitrile.

7. Method in accordance with claim 1 in which the nitrile is selected from the group consisting of acetonitrile, butyronitrile, caprylonitrile, isovaleronitrile, tridecanitrile, benzonitrile, O-methylbenzonitrile, O-tolunitrile, naphthylnitrile, cyclohexylbenzonitrile, cyclohexylnitrile, phenylbutyronitrile, phenylacetonitrile.

8. Method in accordance with claim 1 in which the naphtha boils between 365 and 405° F., the organic nitrile is caprylonitrile and the nitrile is blended with the naphtha in the amount of 50 parts per million.

References Cited in the file of this patent

UNITED STATES PATENTS

2,235,936	Lerch et al.	Mar. 25, 1941
2,393,212	Young et al.	Jan. 15, 1946