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ODORLESS SOLVENT MANUFACTURE

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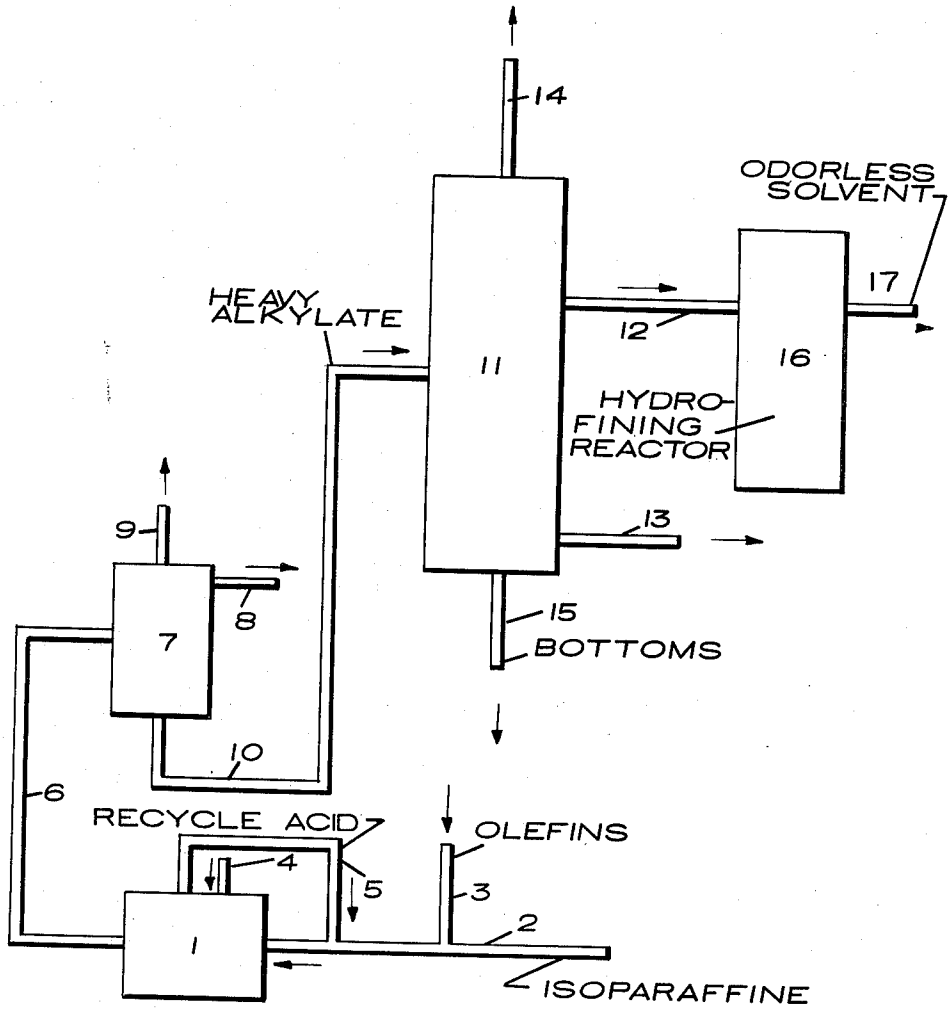

WILLIAM A. JONES
CURVIN H. STEIN INVENTORS

BY W. O. Hilman ATTORNEY

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ODORLESS SOLVENT MANUFACTURE

William A. Jones and Curvin H. Stein, Sarnia, Ontario, Canada, assignors to Esso Research and Engineering Company, a corporation of Delaware

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The present invention is concerned with the production of substantially odorless hydrocarbon solvents. The invention is more particularly concerned with the preparation of hydrocarbon solvents from a heavy alkylate product. In accordance with the present invention a high quality substantially odorless hydrocarbon solvent is secured by distilling a heavy alkylate product followed by hydrofining the desired fraction.

It is well known in the art to prepare hydrocarbon solvents by various procedures. For instance it is known that odorless hydrocarbon solvents are mainly isoparaffins and paraffins boiling in the range from about 350° to 450° F. However, when these solvents are prepared from an alkylate material, they are characterized by a rancid odor. This odor is not eliminated during distillation to separate solvents of the desired boiling ranges and distillation actually causes the solvents to acquire additional rancid odor which cannot be removed by ordinary treating methods such as caustic washing, acid washing or percolation through clay. In accordance with the present invention this rancid odor is overcome by hydrofining the desired alkylate cut.

The process of the present invention may be fully understood by reference to the drawing illustrating one embodiment of the same.

Referring specifically to the drawing, a feed stream comprising isoparaffins such as isobutane or isopentane is introduced into alkylation zone **1** by means of feed line **2**. Olefins such as C_2–C_5 monoolefinic hydrocarbons are introduced into the isoparaffins by means of line **3** while acids are introduced into alkylation zone **1** by means of line **4**. Preferred reactants comprise isobutane and C_4 olefins. Recycle is illustrated by means of line **5**. The alkylation operation comprises a conventional one wherein the ratio of isoparaffins to olefins is maintained relatively high in order to prevent polymerization of the olefins, while the concentration of the acid, preferably sulfuric acid, is in excess of 88%, preferably in excess of 96%. Temperature conditions are in the range from 30° F. to 100° F., while the time of reaction is generally about 10–60 minutes. It is to be understood that alkylation zone **1** may comprise any suitable number and arrangement of stages, settling zones and the like.

The alkylate product is withdrawn from alkylation zone **1** by means of line **6** and introduced into a distillation zone **7** wherein a light alkylate product boiling in the range below about 350° F. is segregated by means of line **8**. Hydrocarbon constituents boiling below the gasoline boiling range are removed overhead by means of line **9**. A heavy alkylate product boiling above about 350° F. is removed by means of line **10** and introduced into a distillation zone **11**. Temperature and pressure conditions are adjusted in distillation zone **11** to remove as a side stream by means of line **12** an alkylate product boiling in the range from about 350° to 400° F. A second side stream boiling in the range from 400° to 450° F. is removed by means of line **13**. Hydrocarbon constituents boiling below about 350° F. are removed overhead by means of line **14** while constituents boiling above about 450° F. are removed by means of line **15**. The alkylate products of either or both lines **12** and **13** may be processed in accordance with this invention.

In accordance with the present invention the segregated alkylate stream intended for use as an odorless solvent is passed to hydrofining reaction zone **16** to be subjected to mild hydrofining conditions as described hereinafter. As will be appreciated, the stream of line **12** is passed through a heating zone prior to entrance to the hydrofining zone to raise the stream to hydrofining temperatures. The finished odorless solvent is removed by means of line **17** as a high quality product solvent.

It is essential, in practicing the present invention that the hydrofining operation conducted on the alkylate fraction be a "mild hydrofining operation." This is to be distinguished from conventional hydrofining operations heretofore practiced in the art. Such hydrofining operations have been employed at pressures from 200 to 500 lbs. per square inch, at feed rates of .5 to 2.0 volumes of feed per volume of catalyst per hour. Relatively high rates of hydrogen recycle have been employed, for example, 2,000 to 4,000 standard cubic feet per barrel in order to vaporize the feed, to control heat developed by hydrogen addition and prevent carbonization of the catalyst. Likewise, temperatures above 700° F. have been used, normally, in order to vaporize the feed, convert high molecular weight hydrocarbons to lower molecular weight or to remove high percentages of sulfur. Under these conditions, hydrogen consumption has generally been in the range of 150 to 600 standard cubic feet per barrel of feed for desulfurization and above 1,000 cubic feet per barrel for hydrogenation-cracking. This relatively high consumption of hydrogen has made the process expensive to operate, so that where ample supplies of crude oils containing light hydrocarbons exist, its application has been limited to the treatment of relatively high sulfur stocks which could not be desulfurized by any other available treating operation.

The "mild hydrofining" condition of the present invention may be carried out by lowering the temperature, increasing the feed rate per volume of catalyst or by using a less active catalyst. In accordance with the present invention the temperatures used are in the range from about 300° to 700° F., preferably in the range from about 500° to 650° F. Pressures employed are in the range from 50 to 1000 lbs. per square inch, preferably in the range from about 200 to 800 lbs. per square inch. The feed rates, in accordance with the present process, are in the range from about 0.5 to 10 volumes of liquid per volume of catalyst per hour. Preferred feed rates are in the range from 1 to 5 v./v./hr. The hydrogen in the gas to the hydrofining unit may vary from 50 to 100%. This means that, for example, dilute hydrogen from a hydroformer can be used in the hydrofining process. Since the treatment is effective with the oil maintained at least partially in the liquid phase, hydrogen recycle rates above 1,000 cubic feet per barrel of feed oil have not been found necessary to prevent carbonization of the catalyst.

The catalyst utilized in the present operation may comprise known hydrofining catalysts, as for example, nickel on kieselguhr, platinum on alumina, molybdenum oxide or sulfide on alumina, cobalt molybdate on alumina, nickel-tungsten sulfides and other catalysts known in the art. While the preferred catalyst of the present invention comprises cobalt molybdate on alumina, catalysts such as nickel on kieselguhr and nickel-tungsten sulfides have been found effective in the mild hydrofining operation to be conducted in accordance with this invention. In the preferred catalyst the amount of cobalt oxide is

about 4% to 5% and of molybdenum oxide about 8% to 10% based on the weight of the alumina. The catalyst is prepared by known methods, such as by impregnation of the alumina with a water-solution of cobalt molybdate or of other water-soluble salts of cobalt and molybdenum followed by heating to convert the cobalt molybdate and the salts to their oxides. The catalyst may also be prepared by coprecipitation of aluminum, cobalt and molybdenum hydroxides by addition of an ammoniacal solution of ammonium molybdate to an acid solution of a cobalt salt and an aluminum salt followed by water washing and by heating to convert to the oxides. Catalysts prepared by dry mixing of alumina, cobalt oxide and molybdenum trioxide may also be used. The catalyst may be used in the form of pills, broken stones or other suitable forms.

The mild hydrofining may be carried out by contacting alkylate and hydrogen with the catalyst either by batch or by continuous flow operation. In batch operation the oil and the desired proportion of catalyst to oil, under a hydrogen atmosphere at the required pressure, are heated to the required temperature in a bomb or autoclave and mixed together for the required time by stirring or by shaking.

In continuous operation, the oil and hydrogen are contacted with catalyst by continuous flow through a vessel packed with catalyst. The oil feed to the reactor is preheated to the required temperature by means of a furnace or similar means. Hydrogen may or may not be heated prior to feeding to the reactor depending on the quantity used. The degree of contact of oil saturated with hydrogen with the catalyst is determined by the ratio of the oil flow rate to the catalyst volume.

After the hydrofining process has been carried out by either the batch or continuous technique described, a small portion of the lighter reactor effluent is separated. This may be achieved in a simple still in which pressure is dropped sufficiently to "flash" about 1–2% of the hydrofined alkylate product. Hydrogen is thereby separated from the alkylate product together with about 90% to 95% of the by-product gases formed as a result of the hydrofining. The disengaged hydrogen may be purified for recycle.

The residual traces of H_2S in the hydrofined product may be eliminated if necessary by caustic washing. A single stage treatment using about 2 to 5 weight percent of about 5° Bé. caustic is satisfactory.

It is to be understood that the mild hydrofining conditions of the present invention are secured by the selection of the catalyst and by adjustment of the space velocity, temperature and pressure. For instance, if a relatively high liquid feed rate is used as compared to the amount of catalyst present (high space velocity) the higher temperature range indicated may be employed. On the other hand, if a very active catalyst is used, it may be desirable to use a relatively high feed rate together with a relatively low temperature. The mild hydrofining conditions of the present invention are best measured by the amount of hydrogen consumed. In the process of this invention, the hydrofining conditions are adjusted to secure a positive consumption of hydrogen but not more than 10 standard cubic feet per barrel not including mechanical losses. There is substantially no change in the inspections of the alkylate so that the hydrofining operation does not appreciably alter the viscosity, specific gravity, boiling range, or aniline point of the alkylate. Nevertheless, this mild hydrofining treatment results in the desired improvement in the odor of the alkylate by a mechanism which is not fully understood.

Another means of establishing the mild hydrofining conditions to be employed is to so adjust the temperature, pressure, and feed rates so that over 98% of the hydrofined products is of the same flash point as the original feed. Generally, conditions are so adjusted that less than 2% of the hydrofined constituents are converted to lower

boiling constituents. The following examples demonstrate the utility and operability of this invention:

Example 1

A sample of the 350° to 400° F. cut of batch distilled heavy alkylate was given a 10 volume percent 10° Bé. caustic wash and then hydrofined under the following conditions:

Pressure..... 600 p. s. i. g.
Temperature... 550° F.
Catalyst..... UOP Nickel, 1 vol. percent on oil charge.
Time..... 10 hours.

This treatment removed the rancid odor present in the caustic washed feed.

Inspection	Feed	Product
Odor	Unsatisfactory	Satisfactory.
°API Gravity	54.0	54.2.
Wt. Percent Sulphur	0.002	0.002.
Aniline Pt., °F	181	187.
K. B. S. V.	26	26.
R. I. @ 20° C	1.4247	1.4243.
Bromine No	3	Less than 1.
ASTM Distillation:		
IBP	351	350.
10%	355	355.
50%	361	361.
90%	368	368.
FBP	378	378.

Example 2

Feed..... Same as (1) except no caustic wash.
Unit..... Continuous upflow.
Catalyst..... Cobalt molybdate on alumina.
Pressure..... 770 p. s. i. g.
Temperature..... 575° F.
V./v./hr. 1.0
Excess H_2..... 220 c. f./bbl.
Hydrogen consumption..... Less than 10 s. c. f./barrel of feed.

This hydrofining treatment removed the rancid odor of the feed stock.

Inspections of feed and product are:

Inspection	Feed	Product
Odor	Unsatisfactory	Satisfactory.
°API	54.0	54.5.
Flash Pt., °F	130	124.
Color Saybolt		+30.
Wt. Percent Sulphur	0.002	0.002.
Bromine No	2.8	Less than 1.
Aniline Pt., °F	181	181.5.
R. I. @ 20° C	1.4247	1.4244.
ASTM Distillation:		
IBP	350	350.
10%	354	354.
50%	359	359.
90%	369	366.
FBP	380	378.

The data of these examples, shows that the rancid odor of an alkylate product cannot be eliminated by caustic washing. However, the odor can be eliminated by a mild hydrofining treatment of the character identified.

What is claimed is:

1. Improved process for the preparation of a high quality essentially odorless hydrocarbon solvent which comprises alkylating an isoparaffin with an olefin, segregating a fraction of the alkylate product boiling in the range from about 350° to 450° F., and thereafter mildly hydrofining said fraction at conditions to secure a positive consumption of hydrogen but less than 10 standard cubic feet per barrel of product.

2. A process for preparing high quality alkylate in which a heavy alkylate fraction is hydrofined at a temperature of about 300° to 700° F., at a pressure of about 50 to 1,000 lbs. per square inch in the presence of excess hydrogen and in contact with a hydrogenation catalyst in a manner to secure a hydrogen consumption less than 10

standard cubic feet per barrel of feed whereby the normally rancid odor of the alkylate is removed with substantially no change in other properties.

3. The process of removing undesirable odor of a heavy alkylate boiling within the range of about 350° to 450° F., comprising hydrofining said alkylate to secure a positive hydrogen consumption of not more than 10 standard cubic feet of hydrogen per barrel, segregating H_2 along with other gaseous by-products and less than 2% of the

lighter alkylate constituents, and caustic washing the final alkylate product.

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