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REFINING AROMATIC DISTILLATES

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This invention relates to a process of refining toluene and more particularly it relates to the refining of toluene of the so-called "nitration grade." One object of the process is to refine nitration grade toluene to such an extent that it will remain color stable and will pass the acid wash test after prolonged handling and storage. Another object of the invention is to restore the color of refined toluene which has gone off color in storage. Still another object of the invention is to provide a process for refining toluene and making it color stable without adding materially to the cost of the refining treatment or losses of toluene.

Heretofore it has been the practice in making nitration grade toluene to subject the crude toluene to treatment with strong sulfuric acid. For this purpose sulfuric acid having a concentration of 87 to 98 percent H_2SO_4 has generally been used, the amount employed being about 5 to 10 pounds per barrel or more, for example 20 to 40 pounds per barrel depending on the character of the crude toluene and the amount of impurities which must be removed from it. The treatment is usually carried out at ordinary temperature, e. g. 80 to 90° F. After treating, the toluene is separated from the acid sludge, neutralized with caustic, and redistilled. Toluene produced in this way when carefully fractionated forms the the base stock from which trinitrotoluene is produced by nitration.

The foregoing is a brief outline of the method which has long been employed in the coal tar industry for making nitration grade toluene from coal distillates and from light oils absorbed from coal distillation gases. However, when this method was applied to the manufacture of nitration grade toluene obtained by the catalytic treatment of petroleum napthas, difficulty was encountered with color stability of the product. In making toluene from petroleum napthas, it is generally the practice to fractionate from the naptha a cut boiling in the range of about 180 to 275° F. (toluene boils at 232° F.) and subject this stock to hydroforming in the presence of a hydroforming catalyst, for example an oxide of a sixth group metal deposited on active alumina. Active alumina promoted with about 5 to 10 percent of molybdenum oxide is a very good catalyst. In carrying out this operation the naptha vapors are passed into contact with the catalyst at a space velocity of about 0.2 to 5 volumes of liquid naptha per hour per volume of catalyst at a temperature in the range of about 900 to 1100° F. and a pressure of about 100 to 400 pounds per square inch. Hydrogen or hydrogen-containing gas is simultaneously charged with the naptha in an amount of about 500 to 4000, generally about 2500, cubic feet per barrel of naptha charged.

The product of this hydroforming reaction may contain from 5% to 20% of toluene, the concentration depending on the efficiency of the catalyst, the character of the naptha and other factors. If attempts are made to separate the toluene by direct fractionation, azeotropic mixtures are obtained containing excessive non-aromatics to permit its use in TNT manufacture. In general, there is sufficient contamination of the toluene fraction with aliphatic hydrocarbons to necessitate an extra refining step to effect a separation of nitration grade toluene. For this purpose solvent distillation may be used, for example, distillation in the presence of a polar solvent such as cresol, phenol, furfural, chlorex, nitromethane, etc. From this operation a crude toluene is obtained in a high concentration, generally above 98 percent. Further refining is necessary, however, to remove small amounts of certain impurities, particularly olefine hydrocarbons. If these impurities are allowed to remain in the toluene undesirable reactions occur in TNT manufacture which produces an unstable TNT. The impurities are readily indicated by the so-called "acid wash test," U. S. Army Specification 55–11–38C—sect. E5 according to which a sample of the toluene is treated with sulfuric acid and the amount of color development is noted. The color obtained in this way is known as the "acid wash color." The test consists in shaking a small sample of toluene with 96% H_2SO_4 and noting the color of the acid in comparison with certain color standards.

When it has been attempted to refine petroleum toluene by treatment with sulfuric acid in the manner outlined hereinabove, using sufficient sulfuric acid to meet the requirements for nitration grade toluene, difficulty has been encountered in many cases with acid wash color instability. The toluene after acid treating, for example with 5 pounds per barrel of 98% H_2SO_4 followed by caustic washing and distillation, has given satisfactory acid wash color, when freshly prepared but after a period of time the acid wash color has progressively increased, indicating a deterioration in handling and storage. The cause of this deterioration is quite obscure, and has been explained to be due to traces of unattacked olefine or due to decomposition of alkyl sulfates or sulfonates during the redistillation step following caustic washing. In fact it is not easy to under-

stand how color-forming, unsaturated substances could escape the vigorous acid treatment, which suggests that the acid treatment itself may, in some way, be responsible for the color instability as a result of some secondary action.

I have now discovered that if the refined toluene from the acid treating operation is further treated with a very small amount of maleic anhydride or maleic acid, the acid wash color is stabilized to a remarkable degree. Furthermore, if acid refined toluene has already deteriorated in storage, to a point where it fails to meet acid wash color requirements, the acid wash color may be improved, i. e. reduced, by the maleic anhydride treatment. The amount of maleic anhydride required for treating acid refined toluene is exceedingly small, less than .05%, and generally within the range of .001% to .01%. The cost of the treatment is therefore quite low notwithstanding the fact that the reagent is relatively expensive.

As an example of the color instability of acid treated hydroformer toluene, the following table shows the acid wash color after various periods of rapid aging. Each sample was treated with the amount and concentration of sulfuric acid indicated, the toluene being thoroughly agitated with the acid for the time specified. In commercial practice the time of agitation is about 30 seconds. After the treatment, each sample was separated from acid, washed, neutralized with caustic soda and redistilled before testing.

Time of contact	Acid wash color			
	Initial	After aging		
		4 hrs.	8 hrs.	16 hrs.
3 LBS. 98% SULFURIC ACID PER BARREL OF TOLUENE				
2 min.	1	3-4	5-6	6+
5 min.	0-1	0-1	1	3-4
5 LBS. 98% SULFURIC ACID PER BARREL OF TOLUENE				
1 min.	1	2	3-4	5-6
2 min.	0-1	0-1	0-1	0-1
5 LBS. 93% SULFURIC ACID PER BARREL OF TOLUENE				
2 min.	1-2	1-2	3-4	4

The rapid aging referred to was carried out according to the following accelerated test procedure:

A 600 ml. sample of toluene is placed in a three-necked round bottom 1000 ml. Pyrex flask. The flask is connected thru a ground joint to a reflux condenser and placed on a boiling water bath. A slow current of air is led into the flask, the air having been purified by passing thru 98% sulfuric acid, solid potassium hydroxide and then thru Drierite. Before entering the flask the air passes thru eight feet of copper tubing submerged in the boiling water bath.

Samples of toluene are withdrawn from the flask at intervals up to twenty-four hours or until the acid wash color of the sample reaches 6+. If the sample does not become darker than 6 color in 8 hours, it is believed that the shipment will arrive at the nitration plant with an acid wash color of better than 4.

Another lot of crude toluene was acid treated with 98% sulfuric acid, neutralized with caustic solution, and redistilled. After setting aside a portion as a control sample, a second portion was treated with 0.01% maleic anhydride for 15 minutes, and a third portion was similarly treated with maleic acid. Both samples were then washed with caustic to remove reaction products and excess treating agent. The initial acid wash color and color stability of the three samples was as follows:

	Acid wash color			
	Initial	2 hrs.	4 hrs.	6 hrs.
Control sample	2	3	5+	6+
Control+.01% maleic acid	2	2-3	2	2
Control+.01% maleic anhydride	1	1-2	0-1	0-1

Another lot of toluene treated with sulfuric acid as just described was further treated with a very small amount of maleic anhydride which was added to the toluene and thoroughly mixed therewith. The toluene was then allowed to stand for a short time at ordinary temperature and then the maleic anhydride and reaction products were removed by washing the toluene with a caustic alkali solution. A moderately elevated temperature, for example 100 to 150° F., can be used for the maleic anhydride treatment. No redistillation was necessary after this treatment. As an example of the results obtained, toluene with an initial acid wash color of about 1 to 2 had an acid wash color of 1 after treatment for two minutes with .01 percent maleic anhydride and approximately the same color was obtained on another sample treated for one hour with maleic anhydride. Another lot of toluene having an initial acid wash color of 4 to 5 was treated with .01 percent maleic anhydride for periods varying from two to thirty minutes at 80 to 90° F., after which the toluene had an acid wash color of 3 to 4, regardless of the treating time employed. Another sample of the same stock having an acid wash color of 4 to 5 was treated successively with 0.1 percent portions of maleic anhydride for periods of 30 minutes and 15 minutes respectively, at a temperature of 89° F. The acid wash color of the stock was then 2 to 3.

In another series of experiments, a quantity of crude toluene was treated with about five pounds per barrel of 98% sulfuric acid, neutralized and distilled. Samples of this stock were then treated with maleic anhydride in two concentrations, .01% and .005%, and thereafter washed with caustic soda solution. These samples were tested for initial acid wash color by the acid wash test and also for acid wash color stability after exposure to ultraviolet light, used as an alternative aging test, with the following results:

	No treatment	.01% M. A.	.005% M. A.
Initial acid wash color	3-4	2	2
Ultraviolet stability: Exposure time—			
20 min.	4-5	2-3	2-3
40 min.	5	2-3	2
80 min.	5-6	2	2-3

These data indicate that with this stock the stabilizing effect of maleic anhydride is quite marked and little difference in stability was obtained by doubling the amount used in the treatment.

In cases where the amount of acid treatment was insufficient to produce a toluene product of satisfactory color stability, treatment with maleic anhydride in an amount of .01% for one hour at room temperature gave a product of excellent stability as indicated by the following data:

	Acid refined	Acid refined and maleic anhydride treated
Initial acid wash color	1-2	1+
Untraviolet stability:		
Exposure time—		
20 min.	4	1-2
40 min.	4-5	1-2
80 min.	4-5	1-2

When the maleic anhydride treatment was continued for only two minutes instead of one hour, slightly less stable products were obtained.

When applying my process to the refining of toluene, it should be understood that the process may be employed as a supplement to the ordinary acid treating process for increasing the color stability of toluene or I may reduce the amount of acid treating by the use of the maleic acid-anhydride treatment, thereby increasing the yield of toluene and reducing chemical costs. In the ordinary acid treatment, for example, employing 10 pounds of 98% acid per barrel, losses of toluene thru sulfonation alone have been found to be over seven barrels per thousand barrels of stock treated. In addition to this loss there is the formation of acid sludge of indeterminate composition. If sulfuric acid of lower concentration is employed, e. g. 88 to 93%, and color stability is obtained by the application of maleic anhydride, in accordance with my process, a substantial reduction in loss of toluene by sulfonation is obtainable.

The term "maleic acid" as employed in the claims includes both the acid and its anhydride.

Although I have described my invention with respect to certain specific applications thereof, it should be understood that the invention is not to be limited thereby. Thus the process of refining with maleic acid may be applied to other aromatic distillates besides toluene; for example, it may be applied to aromatic varnish and lacquer solvents, xylene, etc., particularly aromatic distillates derived from the conversion of petroleum oils under aromatizing conditions.

I claim:

1. The process of improving the acid wash color stability of acid refined toluene which originally possessed a satisfactory acid wash color but which has deteriorated in storage which comprises treating said deteriorated toluene with a small amount of maleic acid in the range of above .005% and below 0.1% based on the weight of toluene treated.

2. The process of stabilizing the acid wash color of nitration grade toluene prepared from petroleum naphtha by subjecting it to the action of a hydroforming catalyst at about 900 to 1100° F. in the presence of about 500 to 4000 cubic feet of hydrogen per barrel of naphtha and a pressure of about 100 to 400 p. s. i., fractionating the product with the aid of a polar solvent to recover therefrom a fraction containing a high concentration of toluene, and subjecting said toluene fraction to treatment with concentrated sulfuric acid in the proportion of about 3 to 10 pounds per barrel, resulting in a product unstable with respect to acid wash color, said process comprising treating said acid-refined toluene with about .05 to .001 per cent of maleic acid thereby rendering said toluene satisfactory for nitration as indicated by the acid wash color test.

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