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CHEMICAL COMPOSITION

Allen R. Jones, Elizabeth, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

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This invention relates to the stabilization of aromatic amines against deterioration, etc., during storage.

Aromatic amines such as aniline, toluidine, xylidine, etc., are normally substantially colorless when freshly prepared or freshly distilled, but tend to darken in color during storage, the undesirable results being greatly accelerated by storage at elevated temperatures.

The object of the present invention is to stabilize such aromatic amines against discoloration during storage.

Broadly, the invention comprises adding to the aromatic amines a small amount of a stabilizer comprising essentially an alkylene polyamine, which may be considered as having the general formula, $NH_2(RNH)_nRNH_2$, where R represents an alkylene group, such as ethylene, propylene, butylene, etc., and n represents a number from 0 to 5, and preferably 1 to 3. One particular alkylene polyamine which has been found very satisfactory is diethylene triamine,

$$(NH_2.C_2H_4)_2NH$$

Another is triethylene tetramine,

$$(H_2N.CH_2.CH_2.NH.CH_2)_2$$

The first member of this series is ethylene diamine, $NH_2.C_2H_4.NH_2$, in which case n is equal to zero.

Although the amount of the stabilizer to be used may vary according to the intended duration of storage and the temperature of storage, as well as according to the particular aromatic amines and the particular stabilizer used, in general about .01% to 0.5% of stabilizer will be sufficient, and usually about .02% to 0.2% by weight of stabilizer will be found most practical for giving satisfactory results. The preferred proportions are about .05% to 0.1% of stabilizer.

Although the invention is intended to apply broadly to the stabilization of any type of aromatic amines, it is believed particularly applicable to alkaryl amines, especially those having from 1 to 3 alkyl carbon atoms. The invention has been found very successful for the stabilization of xylidine, either the pure separate isomers or mixtures thereof, or relatively crude or partially or highly refined commercial products containing same. The xylidines have the general chemical formula $(CH_3)_2C_6H_3NH_2$. Other alkaryl amines which may be stabilized include the toluidines, ortho, meta or para, or mixtures thereof, the several ethyl anilines, cumidine (which is isopropyl aniline), etc. Dialkylated or trialkylated

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aryl amines are preferred. Although the invention is particularly applicable to such alkaryl amines, it may also be used for stabilizing aniline, naphthylamines and various derivatives of aniline in which either or both of the hydrogens of the amino group are substituted by hydrocarbons, i. e., either alkyl or aryl groups, e. g., in N-monomethyl aniline, N-dimethyl aniline, N-monoethyl aniline, etc. Thus, although the invention is particularly applicable to alkaryl primary amines, other amines such as secondary and tertiary amines may also be used. Also alkaryl primary and secondary diamines, such as N,N'-di-butyl-p-phenylene diamine, may be used. The invention applies to alkaryl amines made by any process, including hydrogenation from the corresponding nitro compounds.

The various above described aromatic amines may be used alone, for example, as a dye intermediate where color is particularly objectionable or together with a diluent such as a hydrocarbon solvent, e. g., naphtha or gasoline for use as motor fuel. The alkaryl amines, e. g., xylidine, are particularly valuable for their anti-knock properties in motor fuels, either with or without lead alkyl anti-knock agents, e. g., tetraethyl lead. The aromatic amines may also be diluted with alcohols, ether or other organic solvents to form mixtures suitable for de-icing and knock suppression in aircraft engines. Such diluents may be present in amounts ranging from only a few per cent up to 10, 20 or even 100 times the volume of the aromatic amines.

In carrying out the invention, it is preferred to add the stabilizer to the aromatic amines as soon as the latter has been prepared, or immediately after distillation, preferably carried out under an inert atmosphere, such as nitrogen, so that a water white distillate is obtained for stabilization. This latter condition, however, is not essential to the operation of the invention.

The following experimental data will illustrate the advantages of the invention.

The commercial xylidine, which consisted of a mixture of various isomers, and which had been prepared by hydrogenation of a nitroxylene, and which had been freshly distilled in an atmosphere of nitrogen, was subjected alone, and together with various concentrations ranging from .05% to 1.0% by weight of diethylene triamine, to an accelerated stability test which consisted in heating the samples in open bottles in a Staeger-type, rotary-tray, oven, maintained at 70° C. (+ or −1° C.), and examining the color of the samples by the optical density method,

using a North Sky filter in the Hellige-Diller photoelectric colorimeter, at the start of the test, and at various times thereafter periodically until each sample became degraded in color to an optical density of at least 1.00 (10% light transmission). This optical density is the maximum which xylidine can have if it is to be blended into aviation gasoline, in a concentration ranging up to 3% by volume, and not cause a change in the appearance of the gasoline. The optical density reported herein is referred to water as the standard and is directly proportional to the concentration of color bodies in the sample. The samples were periodically removed from the oven and tested for optical density with the following results:

Percent Diethylene Triamine added to Xylidine	Optical Density Readings after No. of Hours Shown									
	0	6½	22½	29½	69½	94	100	117	142	165½
.0	0.00	0.03	0.33	0.46	1.16					
0.05	0.00	0.005	0.14	.21	0.515	0.605	0.63	0.70	0.80	0.85
.1	0.00	0.01	0.16	.22	0.52	0.62	0.645	0.71	0.80	0.86
.2	0.00	0.02	0.185	.25	0.58	0.69	0.72	0.79	0.875	0.96
.5	0.00	0.11	0.41	.52	0.86	1.00	1.02	1.11		
1.0	0.00	0.38	0.70	.79	1.22					

It is apparent from these data that the number of hours at 70° C. required to degrade the xylidine to an optical density of 1.00 (10% light transmission) is increased from 60 to over 200 hours with 0.1% or 0.05% by weight of diethylene triamine is added to the xylidine. Since the color degradation of aromatic amines is accelerated by storage at an elevated temperature, the time of the test is equivalent to a much longer period of storage at room temperature to produce the same optical density of the xylidine.

It is not intended that this invention be limited to the particular materials which have been given merely for the sake of illustration, but only by the appended claims in which it is intended to claim all novelty inherent in the invention, as well as all modifications coming within the scope and spirit of the invention.

I claim:

1. A mono-nuclear aromatic hydrocarbon amine stabilized against discoloration during storage by having added thereto about .02% to 0.2% of diethylene triamine.

2. A xylidine stabilized against discoloration during storage by having added thereto about .05% to 0.1% of diethylene triamine.

3. A mono-nuclear aromatic hydrocarbon amine having added thereto a small amount of stabilizer, having the general formula

$$NH_2(RNH)_nRNH_2$$

where R represents an alkylene group selected from the class consisting of ethylene, propylene, and butylene, and n represents a number from 0 to 5.

4. A composition of matter according to claim 3 in which about 0.01% to 0.5% of stabilizer is present.

5. A composition comprising an alkaryl amine having from 1 to 3 carbon atoms having added thereto a small amount of stabilizer having the general formula $NH_2(RNH)_nRNH_2$ where R represents an alkylene group selected from the class consisting of ethylene, propylene, and butylene, and n represents a number from 0 to 5.

6. A composition according to claim 5 in which about 0.01% to 0.5% of stabilizer is present.

7. A composition of matter consisting of a gasoline blended with a mono-nuclear aromatic hydrocarbon amine in concentrations between 0.001% and 3.0% and a stabilizer having the general formula $NH_2(RNH)_nRNH_2$ where R represents an alkylene group selected from the class consisting of ethylene, propylene, and butylene, and n represents a number from 0 to 5, in concentrations between 0.00001% and 0.01%.

8. A composition of matter consisting of a gasoline containing tetra-ethyl-lead up to 6 cc. per gallon, an amino-phenol type gum inhibitor up to 0.001 lb. per gallon, xylidene up to 3% by volume, and a stabilizer for the xylidene having the general formula $NH_2(RNH)_nRNH_2$ where R represents an alkylene group selected from the class consisting of ethylene, propylene, and butylene, and n represents a number from 0 to 5, in concentrations between 0.00001% and 0.01%.

ALLEN R. JONES.

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