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STABILIZED XYLIDINE

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2 Claims. (Cl. 260—578)

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

The alkaryl amines such as 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 alkaryl amines against discoloration during storage.

Broadly, the invention comprises adding to the alkaryl amines a small amount of a stabilizer comprising essentially an organic sulfur compound, preferably of the aryl mercaptan type. Such compounds may, for instance, have the general formula RXH in which R is an aromatic, preferably an alkyl aromatic hydrocarbon radical, and X is an atom selected from the group consisting of sulfur, selenium, and tellurium. Although in such compounds it is preferable that R be a mono-nuclear aromatic radical, i. e., one derived from benzene, poly-nuclear compounds may also be used such as those derived from naphthylene and the like. As mentioned above, it is preferable that the aromatic group R contain one or more alkyl substituents attached to the aromatic nucleus, and in general it is preferable that the radical R contain from 1 to 25 alkyl carbon atoms, preferably 1 to 6 alkyl carbon atoms. One particular stabilizer which has been found particularly satisfactory is parathiocresol which has the formula $CH_3C_6H_4SH$. Other compounds which may be used include ethylthiophenol, propylthiophenol, various butylthiophenols, such as the paratert.-butylthiophenol, etc., as well as higher alkyl phenols, e. g., wax thiophenols (in which an alkyl group corresponding to the wax hydrocarbon molecule is attached to the thiophenol nucleus). Other aromatic sulfur compounds, i. e., ones containing sulfur attached directly to or in an aromatic nucleus, may be used such as mercaptobenzothiazole, heterocyclic S compounds, e. g., thiophene, sulfurized mineral oils, bismercaptomethyl xylol, etc. In addition, the alkyl carbons may be attached to the thiophene nucleus in the form of a number of separate alkyl groups such as exemplified by 2,4 dimethyl 6 tertiary butyl thiophenol.

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 amine and the particular stabilizer used; in general about .01% to 1.0% of stabilizer will be sufficient, and usually about .05% to 0.5% by weight of stabilizer will be found most practical for giving satisfactory results.

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Although the invention is intended to apply broadly to the stabilization of any type of alkaryl amines, it is believed particularly applicable to alkaryl amines 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. 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 and trialkylated aryl amines are preferred. Although the invention is particularly applicable to such alkaryl amines, it may also be used for stabilizing naphthylamines, and the 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.

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. It may also be diluted with alcohols, ethers 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 amine.

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

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

A commercial xylidine, which consisted of a mixture of various isomers, was subjected, alone, and together with 0.2% of parathiocresol, to an accelerated stability test which consisted in heating the samples in open bottles in an oven held at 90° C. and judging color changes by determin-

ing the optical density, using a North Sky filter in the Hellige-Diller photoelectric colorimeter. The following changes in color were observed:

Sample	Optical density (water=0)		
	0 Hrs.	2 Hrs.	4 Hrs.
Commercial xylidines	0.06	0.38	0.73
Ditto+0.2% p-thio cresol	0.05	0.03	0.06

These tests show that the commercial xylidine sample to which 0.2% of parathiocresol had been added did not undergo any substantial change in color even with 4 hours of heating under the severe conditions of this accelerated stability test, whereas the sample of xylidine without stabilizer shows a tremendous darkening in color even after only 2 hours of heating.

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 xylidine stabilized against discoloration during storage by having added thereto about 0.2% of parathiocresol.

2. A xylidene stabilized against discoloration during storage by having added thereto .05% to 0.5% of parathiocresol.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,917,073	Stewart	July 4, 1933
1,947,578	Bond	Feb. 20, 1934
1,961,097	Cunningham	May 29, 1934

FOREIGN PATENTS

Number	Country	Date
432,480	Great Britain	July 22, 1935

OTHER REFERENCES

Chem. Abstracts, vol. 28 (1934), pp. 1335, 5418; *ibid.*, vol. 32 (1938), pp. 2092–3; *ibid.*, vol. 33, col. 2498.