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STABILIZATION OF AMINES WITH 2-ALKYL-4 ALKOXYPHENOLS

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This invention relates to the stabilization of amines and more particularly to a method of preventing the discoloration and other undesirable deterioration which amines or solutions of amines, and particularly aryl amines, undergo upon exposure to air and/or light.

Aryl amines and particularly solutions containing aryl amines become discolored upon standing when exposed to air, and it is an object of the present invention to prevent the discoloration.

The present invention is particularly applicable to the treatment of aryl amines and may also be utilized for preventing the discoloration of aliphatic amines. However, aliphatic amines in general do not readily undergo discoloration and usually are satisfactory for use without the necessity of adding an inhibitor.

Aryl amines are utilized for many purposes, such as intermediates in the preparation of various chemical compounds or as additives to hydrocarbons or other organic materials. In many cases the discoloration of the amines is undesirable and renders the amines unsatisfactory for the desired use.

In a broad aspect the present invention relates to a method of preventing the discoloration of amines which comprises adding thereto a small but effective amount of an inhibitor comprising a 2-alkyl-4-alkoxyphenol.

In another aspect of the present invention relates to a novel composition of matter comprising an aryl amine and an amount of a 2-alkyl-4-alkoxyphenol of usually less than 1% and preferably of from about 0.01 to about 1.0%.

In one specific embodiment the present invention relates to a method for preventing the discoloration of xylidine which comprises adding thereto an amount of 2-tertiary butyl 4-methoxyphenol of usually less than 1% and preferably about 0.05 to about 0.5%.

Various well known inhibitors which have been heretofore proposed for other uses, such as preventing discoloration or gumming in gasolines, have proved unsatisfactory for preventing the discoloration of aryl amines and in some cases these materials have actually accelerated the discoloration of amines. We have now discovered that 2-alkyl-4-alkoxyphenols are particularly effective in preventing the discoloration of amines.

It is understood that the different individual compounds which may be prepared and utilized in accordance with the present invention are not necessarily exactly equivalent in their effectiveness in preventing the discoloration of amines. It is further understood that this effectiveness is

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in part dependent upon the amount of the inhibitor employed. In general, larger amounts of the inhibitor will produce best results, but it is usually unnecessary and undesirable to employ the inhibitor in concentration of greater than 1%.

The inhibitor of the present invention comprises a 2-alkyl-4-alkoxyphenol in which the alkyl group substituted in the ring may comprise any suitable alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, t-butyl, amyl, isoamyl, secondary amyl, etc. Of these groups the tertiary alkyl group appears to be more effective in contributing to the inhibitor potency of the resultant compound than do those groups of lower molecular weight. The substituent alkyl group is preferably in the position ortho to the hydroxyl group, although some compounds in which the substituent group is in the meta position may also have inhibiting value.

We have found that when the alkoxy or ether group is in the 4-position, compounds having greater potency are available than when this group is in any other position in the substituted phenol. The alkyl group of this alkoxy substituent may comprise for example ethyl, methyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, t-butyl, amyl, isoamyl, secondary amyl, t-amyl, etc. groups. Of these, the groups of relatively low molecular weight, comprising methyl or ethyl groups appear to have the strongest influence, although other groups have considerable value. Straight-chain alkyl substituents of greater length than two carbon atoms tend to produce inhibitors of lower potencies than when methyl or ethyl groups are substituted.

The alkyl substituents may be introduced into the aromatic nucleus in a number of ways. One of these consists in alkylating a hydroquinone ether by contacting it at a temperature of 75–80° C. with the alcohol corresponding to the group to be substituted, using 85% phosphoric acid as the catalyst. The reaction mixture is stirred continuously until the reaction is complete. The mixture is then washed with water to remove remaining acid and is extracted with 10% sodium hydroxide solution to remove the unreacted hydroquinone ether. The insoluble portion is distilled under reduced pressure and the resulting compound may be further purified by recrystallization.

The following examples further illustrate the novelty and utility of the present invention but not with the intention of unduly limiting the same. In these examples the relative effectiveness of the inhibitors are measured by the per

cent transmittance, as determined in a Coleman Universal Spectrophotometer, Model 11, after various periods of storage at 70° C.

Inhibitors were added in concentrations of 0.2% by weight to separate portions of technical xylidine and then stored at 70° C. in the presence of air. The solutions were inspected periodically and gave the results reported in the following table:

	Per cent Transmittance @ 550 mu. after—				
	0 Hrs.	5 Hrs.	22 Hrs.	45 Hrs.	96 Hrs.
Xylidine	71	44	7	0	0
Xylidine+0.2% 2-t-Butyl-4-Methoxyphenol	71	70	60	49	5
Xylidine+0.2% 2-t-Butyl-4-Ethoxyphenol	71	70	61	46	3
Xylidine+0.2% 2-t-Amyl-4-Methoxyphenol	71	70	52	28	1

It is to be noted that xylidine alone gave only a 7% transmittance after 22 hours and 0% transmittance after 45 hours. On the other hand, xylidine plus the representative inhibitors of the present invention gave more than 50% transmittance after 22 hours and 49, 46 and 28% transmittance after 45 hours. In interpreting these results, high percent transmittance is an indication that discoloration is retarded since discoloration of the xylidine solution lowers or eliminates transmittance.

We claim as our invention:

1. A method of stabilizing an amine which comprises adding thereto a minor proportion of a 2-alkyl-4-alkoxyphenol.

2. A method of stabilizing an aryl amine which comprises adding thereto a 2-alkyl-4-alkoxyphenol in an amount sufficient to prevent discoloration.

3. A method of stabilizing an aryl amine which comprises adding thereto a 2-alkyl-4-alkoxyphenol in a concentration of from about 0.01 to about 1.0%.

4. A method of stabilizing xylidine which comprises adding thereto a minor proportion of a 2-alkyl-4-alkoxyphenol.

5. A method of stabilizing xylidine which comprises adding thereto 2-t-butyl-4-alkoxyphenol.

6. The process of claim 5 further characterized in that said alkoxy is selected from the group consisting of methoxy and ethoxy.

7. A composition of matter comprising an amine and a 2-alkyl-4-alkoxyphenol.

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