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STABILIZED MONOMERS WITH ALKOXYPHENOLS

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ABSTRACT OF THE DISCLOSURE

Stabilization of acrylic or methacrylic esters using a 4-alkoxyphenol containing fewer than four carbon atoms in the 4-alkoxy group and carrying as substituent on one or both of the 2 and 6 positions a secondary or tertiary alkyl group containing at least four carbon atoms. The 4-alkoxyphenol stabilizer may be, for example, 2,6-ditertiary-butyl-4-methoxyphenol or 2,2'-dihydroxy-3,3'-ditertiary-butyl-5,5'-dimethoxydiphenylmethane.

This invention relates to stabilised monomers and more particularly to acrylic and methacrylic monomers.

It is known that certain substituted phenols are useful as "antioxidants," for example in stabilising rubber, petrol, and edible fats and oils against deterioration due to oxidation reactions. It is also known to use hydroquinone and 4-methoxyphenol (the monomethyl ether of hydroquinone) as polymerisation inhibitors in the storage or transport of acrylic and methacrylic esters. The use of hydroquinone and of 4-methoxyphenol is described, for example, in "Monomeric Acrylic Esters" by E. H. Riddle (Reinhold, New York, 1954). However, not all compounds which are effective as antioxidants are effective in preventing polymerisation of monomers during transport or storage.

We have now found that exceptionally improved storage stability of acrylic and methacrylic esters is provided by addition of a minor proportion of a 4-alkoxyphenol containing fewer than 4 carbon atoms in the alkoxy group and carrying as substituent in one or both of the 2 and 6 positions a secondary or tertiary alkyl group containing at least 4 carbon atoms. These stabilisers have the additional advantage that when used in proportions providing adequate storage stability they need not be removed before the monomer is used in a desired polymerisation reaction. Thus the stabilised monomer may be used in polymerisation reactions initiated by a wide range of polymerisation catalysts without the necessity of a preliminary process of removing the stabiliser by a means such as washing or distillation of the monomer.

Thus according to the present invention there is provided an improved stabilised monomer composition comprising an acrylic or methacrylic ester together with a minor proportion of a 4-alkoxyphenol containing fewer than 4 carbon atoms in the 4-alkoxy group and carrying as substituent in one or both of the 2 and 6 positions a secondary or tertiary alkyl group containing at least 4 carbon atoms.

According to another aspect of the present invention there is provided a process for the polymerisation of an acrylic or methacrylic ester in the presence of a minor proportion of a 4-alkoxyphenol containing fewer than 4 carbon atoms in the 4-alkoxy group and carrying as substituent in one or both of the 2 and 6 positions a secondary or tertiary alkyl group containing at least 4 carbon atoms.

The alkyl substituent in one or both of the 2 and 6

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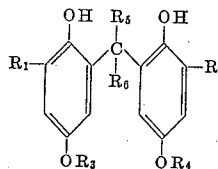
positions may suitably contain, for example, up to 8 carbon atoms.

It is preferred that the alkyl substituent in one or both of the 2 and 6 positions should be a tertiary alkyl group; the tertiary butyl group is especially preferred. Other substituents may also be used, for example the secondary butyl group.

The preferred 4-alkoxyphenols are 4-methoxyphenols. Suitable 4-methoxyphenols include 2-tertiary-butyl-4-methoxyphenol, 2,6-ditertiary-butyl-4-methoxyphenol and 2-secondary-butyl-4-methoxyphenol.

Outstandingly improved stability is obtained when the stabiliser is a 4-alkoxyphenol carrying a tertiary-alkyl substituent in the 2-position and a 2-hydroxy-3-tertiary-alkyl-5-alkoxyphenolmethyl substituent in the 6-position, i.e. when the stabiliser is a 2,2'-dihydroxy-3,3'-ditertiary-alkyl-5,5'-dialkoxy-diphenylmethane.

Suitable 2,2'-dihydroxy-3,3'-ditertiary-alkyl-5,5'-dialkoxy-diphenylmethanes are those represented by the following formula



wherein R_1 and R_2 are tertiary-alkyl groups and may be the same or different; R_3 and R_4 are alkoxy groups or substituted alkoxy groups and may be the same or different; R_5 and R_6 are hydrogen atoms or alkyl groups and may be the same or different.

It is especially preferred to use 2,2'-dihydroxy-3,3'-ditertiary-butyl-5,5'-dimethoxy-diphenylmethane, which may be regarded as two molecules of 2-tertiary-butyl-4-methoxyphenol linked together in their 6-positions by a methylene group.

The proportion of the stabiliser to be used may be, for example, in the range 0.25 to 100 parts by weight per million parts by weight of the monomer. Proportions below the said range may, however, provide a useful improvement in stability in some cases. Proportions above the said range may be used when extremely high storage stability is required but such higher proportions may interfere to some extent with the subsequent polymerization reaction. In general we prefer to use from 0.5 to 5 parts by weight of the stabiliser per million parts by weight of the monomer.

The substituted 4-alkoxyphenols as defined herein are especially advantageous when the monomer is methyl methacrylate but may also be used in the stabilisation of other alkyl or alkoxyalkyl acrylates or methacrylates.

In processes for the polymerisation of monomers in the presence of a minor proportion of a stabiliser as defined herein a wide range of polymerisation catalysts may be used, including organic peroxides and hydroperoxides (for example benzoyl peroxide), lauryl peroxide, tertiary-butyl hydroperoxide, azo catalysts in which the valencies of the azo group are attached to different non-aromatic, preferably tertiary, carbon atoms (for example α,α -di-isobutyronitrile) and the water-soluble persulphates and peroxides (for example ammonium persulphate, potassium persulphate and hydrogen peroxide).

The monomer-soluble catalysts are used in bulk polymerisation and granular polymerisation processes; the water-soluble catalysts are used in aqueous emulsion polymerisation processes.

The invention is illustrated but not limited by the following examples, in which the parts are by weight.

Example 1

Methyl methacrylate was freshly distilled and one part of 2,6-ditertiary-butyl-4-methoxyphenol was added as stabiliser to one million parts of the distilled monomer. Samples of the stabilised monomer were stored at 45° C. in sealed glass tubes, an air space being left in the sealed tube. The storage stability, measured as the time elapsed before the occurrence of a marked increase in the viscosity of the sample, denoting the onset of polymerisation, was between 6 weeks and 9 weeks.

By way of comparison, one part of hydroquinone was added to one million parts of another portion of the distilled methyl methacrylate. The storage stability at 45° C. was 10 days.

Also by way of comparison, one part of 4-methoxyphenol was added to one million parts of another portion of the distilled methyl methacrylate. The storage stability at 45° C. was 14 days.

Example 2

The procedure of Example 1 was repeated except that the samples were stored at 35° C.

One part of 2,6-ditertiary-butyl-4-methoxyphenol was added to one million parts of a portion of the distilled methyl methacrylate. The storage stability at 35° C. was 15 weeks.

By way of comparison, one part of hydroquinone was added to one million parts of another portion of the distilled methyl methacrylate. The storage stability at 35° C. was 4 weeks.

Also by way of comparison, one part of 4-methoxyphenol was added to one million parts of another portion of the distilled methyl methacrylate. The storage stability at 35° C. was 6 weeks.

Example 3

The procedure of Example 1 was repeated except that five parts of 2,6-ditertiary-butyl-4-methoxyphenol were added to one million parts of the distilled methyl methacrylate. The storage stability at 45° C. was 20 weeks.

By way of comparison, five parts of hydroquinone were added to one million parts of another portion of the distilled methyl methacrylate. The storage stability at 45° C. was 3 weeks. Also by way of comparison, five parts of 4-methoxyphenol were added to one million parts of another portion of the distilled methyl methacrylate. The storage stability at 45° C. was between 6 and 8 weeks.

Example 4

The procedure of Example 1 was repeated except that one part of 2,2'-dihydroxy-3,3'-ditertiary-butyl-5,5'-dimethoxy-diphenylmethane was added to one million parts of the distilled methyl methacrylate in the absence of any other added stabiliser. The storage stability at 45° C. was between 90 and 100 days.

Example 5

The procedure of Example 1 was repeated except that five parts of 2-secondary-butyl-4-methoxyphenol were added to one million parts of the distilled methyl methacrylate in the absence of any other added stabiliser. The storage stability at 45° C. was 24 weeks.

Example 6

The procedure of Example 1 was repeated except that one part of 2-tertiary-butyl-4-methoxyphenol was added to one million parts of the distilled methyl methacrylate in the absence of any other added stabiliser. The storage stability at 45° C. was between 100 and 120 days.

Example 7

n-Butyl methacrylate was freshly distilled and one part of 2,6-ditertiary-butyl-4-methoxyphenol was added as stabiliser to one million parts of the distilled monomer.

The storage stability at 45° C., measured as described in Example 1, was between 120 and 135 days.

By way of comparison, one part of hydroquinone was added to one million parts of another portion of the distilled n-butyl methacrylate. The storage stability at 45° C. was 7 days.

Also by way of comparison, one part of 4-methoxyphenol was added to one million parts of another portion of the distilled n-butyl methacrylate. The storage stability at 45° C. was 40 days.

Example 8

Ethyl acrylate was freshly distilled and one part of 2,6-ditertiary-butyl-4-methoxyphenol was added as stabiliser to one million parts of the distilled monomer. The storage stability, measured at 80° C., was 12 hours.

By way of comparison the storage stability of the unstabilised monomer, measured at 80° C., was 4 hours.

Example 9

n-Butyl acrylate was freshly distilled and one part of 2,6-ditertiary-butyl-4-methoxyphenol was added as stabiliser to one million parts of the distilled monomer. The storage stability, measured at 100° C., was 75 minutes.

By way of comparison the storage stability of the unstabilised monomer, measured at 100° C., was 30 minutes.

Example 10

The effects of stabilisers on a process for the polymerisation of methyl methacrylate were assessed as follows.

A casting syrup, containing 5 parts by weight of methyl methacrylate polymer dissolved in 100 parts by weight of methyl methacrylate monomer, was polymerised in a glass cell to give a sheet 1/8 inch thick, benzoyl peroxide (0.1% by weight of the syrup) being used as polymerisation initiator. The initial temperature of the syrup was 60° C. The time taken, under standard conditions, for the temperature of the contents of the cell to reach a maximum was taken as a measure of the rate of polymerisation. When the methyl methacrylate monomer contained 5 parts by weight of 2,6-ditertiary-butyl-4-methoxyphenol per million parts by weight of monomer the maximum temperature was reached after 268 minutes.

By way of comparison, when the methyl methacrylate monomer contained 5 parts by weight of hydroquinone per million parts by weight of monomer the maximum temperature was reached only after 337 minutes.

Again by way of comparison, when the methyl methacrylate monomer contained no added stabiliser the maximum temperature was reached after 246 minutes.

Example 11

Casting syrups were polymerised as described in Example 10, except that the resultant sheets were 3/8 inch thick and the initial temperature was 36° C.

When the methyl methacrylate monomer contained 5 parts by weight of 2,6-ditertiary-butyl-4-methoxyphenol per million parts by weight of monomer the maximum temperature was reached after 26 hours.

By way of comparison, when the methyl methacrylate monomer contained 5 parts by weight of hydroquinone per million parts by weight of monomer the maximum temperature was reached only after 49 hours.

Again by way of comparison, when the methyl methacrylate monomer contained no added stabiliser the maximum temperature was reached after 23 hours.

Example 12

Casting syrups were polymerised as described in Example 10, except that the resultant sheets were 1/4 inch thick and the initial temperature was 49° C.

When the methyl methacrylate monomer contained 5 parts by weight of 2,2'-dihydroxy-3,3'-ditertiary-butyl-5,5'-dimethoxy-diphenylmethane per million parts by weight of monomer the maximum temperature was reached after 10 hours.

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By way of comparison, when the methyl methacrylate monomer contained 5 parts by weight of hydroquinone per million parts by weight of monomer the maximum temperature was reached only after 14 hours.

Again by way of comparison, when the methyl methacrylate monomer contained no added stabiliser the maximum temperature was reached after 10 hours.

Example 13

Casting syrups were polymerised as described in Example 10 except that the initial temperature was 54° C. and that α,α -azo-di-isobutyronitrile (0.1% by weight of the syrup) was used as polymerisation initiator.

When the methyl methacrylate monomer contained 5 parts by weight of 2,6-ditertiary-butyl-4-methoxyphenol per million parts by weight of monomer the maximum temperature was reached after 292 minutes.

By way of comparison, when the monomer contained 5 parts by weight of hydroquinone per million parts by weight of monomer the maximum temperature was reached after 335 minutes.

Again by way of comparison, when the monomer contained no added stabiliser the maximum temperature was reached after 278 minutes.

What we claim is:

1. A stabilized composition comprising an alkyl acrylate or methacrylate together with a stabilizing proportion of a 4-alkoxyphenol containing fewer than four carbon atoms in the 4-alkoxy group and carrying as substituent in one or both of the 2 and 6 positions a secondary or tertiary alkyl group containing at least four carbon atoms.

2. A composition as claimed in claim 1 wherein the 4-alkoxyphenol is a 4-methoxyphenol.

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3. A composition as claimed in claim 1 wherein the alkyl group is a tertiary alkyl group.

4. A composition as claimed in claim 3 wherein the alkyl group is a tertiary butyl group.

5. A composition as claimed in claim 4 wherein the 4-alkoxyphenol is 2-tertiary-butyl-4-methoxyphenol.

6. A composition as claimed in claim 4 wherein the 4-alkoxyphenol is 2,6-ditertiary-butyl-4-methoxyphenol.

7. A composition as claimed in claim 1 wherein the 4-alkoxyphenol is a 2,2'-dihydroxy-3,3'-ditertiary-alkyl-5,5'-dialkoxydiphenylmethane.

8. A composition as claimed in claim 7 wherein the 4-alkoxyphenol is 2,2'-dihydroxy-3,3'-ditertiary-butyl-5,5'-dimethoxydiphenylmethane.

9. A composition as claimed in claim 1 wherein the 4-alkoxyphenol is 2-secondary-butyl-4-methoxyphenol.

10. A composition as claimed in claim 1 wherein the proportion of the 4-alkoxyphenol is from 0.25 to 100 parts by weight per million parts of the acrylic or methacrylic ester.

11. A composition as claimed in claim 10 wherein the proportion of the 4-alkoxyphenol is from 0.5 to 5 parts by weight per million parts by weight of the acrylic or methacrylic ester.

12. A composition as claimed in claim 1 wherein the ester is methyl methacrylate.

References Cited

Baker: J. Pol. Sci., 47 issue 149 (1960) p. 498.

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