

1 494 771

PATENT SPECIFICATION

(11) 1 494 771

- (21) Application No. 1673/75 (22) Filed 15 Jan. 1975
(31) Convention Application No. 620/74
(32) Filed 17 Jan. 1974 in
(33) Switzerland (CH)
(44) Complete Specification published 14 Dec. 1977
(51) INT CL² C07F 7/22 C08K 5/58
(52) Index at acceptance

C2J 6

C3P 10D1A 10K4 4D3B1 4K10 E2 PC12X PC20D1 PC20D2
PC20D3 PC3



(54) MONOOCTYL-TIN-MERCAPTIDE STABILIZERS AND MOULDING MATERIALS CONTAINING THEM

(71) We, CIBA-GEIGY AG., a Swiss Body Corporate of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to mono-octyl tin compounds and their use as stabilisers.

It is known that dialkyl-tin bis-mercaptides, particularly those derived from the mercapto-carboxylic acid esters of fairly short-chain alcohols, are excellent stabilisers for PVC and for numerous copolymers of vinyl chloride. In contrast thereto, the monoalkyl-tin tris-mercaptides as such have attained virtually no significance though they have been proposed simultaneously with the dialkyl-tin bis-mercaptides for the stabilisation of PVC; see, e.g. US-PS. 2,641,588 and 2,731,440.

It is also known that the action of the dialkyl-tin sulphur stabilisers can be boosted by admixture of monoalkyltin sulphur stabilisers. The optimum effect is generally assumed to be at 20–30% proportion of monoalkyl-tin constituents (see DT-AS 1,669,899 and Informations Chemie No. 119, page 119, April 1973; H. Nieman). A further increase in the monoalkyl-tin constituent produces a decrease in the effect, according to the view held hitherto.

It is also known to use butylthiostannonic acid as a stabiliser for PVC moulding materials. However, this stabiliser has a relatively slight effect for its high tin content of 49%. Its pulverulent character furthermore makes it difficult to mix it rapidly into the PVC composition and its pronounced tendency to plate out can in addition lead to difficulties in processing. Alongside dioctyl-tin bis-*i*-octylthioglycolate, butylthiostannonic acid has not been able to acquire any significant industrial importance. Further, DT-OS 1,924,858 mentions butyl-tin tris-dodecylthioglycolate in one example (see Table IV) as a co-stabiliser together with organic sulphur compounds.

The effectiveness of the known monoalkyl-tin tris alkylthioglycolates, which contain fairly short-chain alkyl radicals in the ester group, as PVC stabilisers depends to an exceptional degree on the lubricant chosen for the formulation. In most of the lubricant formulations customary at the present time, these stabilisers show a far lower effect than the corresponding dialkyl-tin compounds. This observation applies not only when comparing equal amounts by weight of stabiliser but also when comparing the effect of chemically equivalent amounts. A further very conspicuous fact is that the effectiveness of these mono-alkyl-tin stabilisers frequently even greatly worsens as the amount of lubricants added is increased. Undoubtedly, the relatively slight heat-stabilising effect of the previously known monoalkyl-tin stabilisers as compared to the corresponding dialkyl-tin compounds is the cause why the former are, up to the present, of virtually no commercial significance.

It is desirable, particularly from the progressively more important points of view of economy and ecology, to keep the concentration of heavy metals in plastics products as low as possible. Hitherto, the objective of the development of new tin stabilisers was in most cases to bring about an increased effect through increasing the tin content in the stabiliser. As a result, numerous new products were disclosed which admittedly have an increased effect relative to the amount of stabiliser employed but has an effect which is even reduced if viewed with regard to the amount of tin employed. In the light of the above criteria it is more appropriate to relate the effectiveness of the organo-tin stabilisers to the proportion of organically bonded tin (g of tin/100 g of PVC) and not to the amount of stabiliser (g of stabiliser/100 g of PVC).

It is an object of the present invention to develop organo-tin stabilisers which have a better heat-stabilising action in PVC or copolymers based on vinyl chloride than the previously known tin stabilisers and which

50

55

60

65

70

75

80

85

90

8

accordingly make it possible to reduce the amount of tin in the polymer.

Accordingly, the subject of the present invention are thermoplastic moulding materials consisting of, or based on, vinyl chloride polymers, which can optionally contain further metal stabilisers and/or additives, characterised in that they contain, as the stabiliser, per 100 parts by weight of the polymer, 0.2 to 5 parts by weight of a compound of the formula I



in which R' is an alkyl radical with 12 to 16 carbon atoms or of mixtures of such compounds. A further subject of the present invention is the compounds of the formula I.

Preferably, the materials contain 0.5 to 2 parts by weight of the organo-tin stabiliser, and preferably the octyl radical is n-octyl and R' represents an alkyl radical with 12 to 14 carbon atoms.

Examples of R' are: i-tridecyl, tetradecyl and i-hexadecyl, but dodecyl, tetradecyl and hexadecyl are preferred, as well as the radicals derived from the commercially available mixtures of alcohols known as Alfols ("Alfol" is a Registered Trade Mark) which substantially have alkyl groups with the same number of carbon atoms and are predominantly branched. The alkyl groups are here described as "alfyl", the number of C atoms being shown behind the name, in parentheses.

There can also be used for the moulding materials according to the invention mixtures of the compounds of the formula I with one another; mixtures in equal amount, preferably with up to 50% by weight of the analogous dialkyl-tin compounds, relative to the amount of the stabiliser of the formula I; and/or mixtures with other metal stabilisers. Amongst the other metal stabilisers, those based on organo-tin are preferred. They are employed at most in equal amount, preferably in amounts of up to 50%, relative to the amount of the stabiliser of the formula I. In addition, metal stabilisers, for example stabiliser systems containing calcium/zinc or barium/cadmium, should be mentioned in this context.

The stabilisers for the moulding materials according to the invention are manufactured according to known processes, especially by the reaction of octyl stannonic acid or mono-octyl-tin oxides with mercaptoacetic acid esters, or by reaction of octyl-tin trichlorides with the mercaptoacetic acid esters, in the presence of HCl acceptors.

Examples of mercapto acetic acid esters to be employed are: thioglycolic acid cetyl ester, thioglycolic acid tetradecyl ester, thioglycolic acid dodecyl ester, and thioglycolic acid tridecyl ester.

Vinyl chloride polymers or vinyl chloride

copolymers are used for the moulding materials according to the invention. Suspension polymers and bulk polymers, and emulsion polymers which have been washed and thus of low emulsifier content are preferred. Examples of comonomers for the copolymers are: vinylidene chloride, trans-dichloroethylene, ethylene, propylene, butylene, maleic acid, acrylic acid, fumaric acid and itaconic acid.

The moulding materials according to the invention are manufactured in accordance with known processes by incorporating the stabiliser and, optionally, additional stabilisers into the polymer. A homogeneous mixture of stabiliser and PVC can be produced, for example, with the aid of a twin-roll mixer at 150–210°C. Depending on the end use of the moulding materials, further additives, such as lubricants, preferably montan waxes or glyceryl esters, plasticisers, fillers, modifiers, such as, say, additives for improving the impact strength, pigments and/or light stabilisers can also be incorporated before, or simultaneously with, the incorporation of the stabiliser.

The moulding materials according to the invention can be converted into shaped articles in accordance with the shaping processes customary for the purpose, for example by extrusion, injection moulding or calendering. They can be used particularly advantageously for the manufacture of packaging materials for foodstuffs. For this end use, additionally incorporated stabilisers and/or other additives must of course be physiologically harmless.

Compared to known organo-tin compounds according to the state of the art, the mono-octyl-tin compounds of the formula I have a better heat-stabilising action. This finding is surprising and unforeseeable because the introduction of longer radicals into the ester group of the mono-octyl-tin tris-thiocarboxylic acid ester reduces the tin content and hence the concentration of the actual active group. Furthermore, it is surprising and particularly advantageous that through the choice of certain long-chain alkyl radicals in the ester group the unfavourable dependence on the lubricant, which has already been mentioned, can be eliminated and that the activity of the stabilisers, to be employed according to the invention, in the customary lubricant formulations even exceeds that of the most effective dialkyl-tin stabilisers, including those mixed with monoalkyl-tin stabilisers.

A further advantage of the stabilisers to be employed according to the invention is that where necessary they provide the possibility of processing tin-stabilised vinyl chloride polymers containing plasticizer to give physiologically harmless finished articles, since their toxicity is in certain cases even lower than that of the physiologically harmless di-n-octyl-tin stabilisers.

The examples which follow explain the invention in more detail. The percentages given therein are % by weight.

A) Manufacture of compounds of formula I

Example 1:

Manufacture of octyl-tin tris-(alfyl(14)-thioglycollate) containing some dioctyl-tin compound.

14.9 g of a mixture of 91% of octyl-tin oxide and 9% of dioctyl-tin oxide, and 50.0 g of thioglycollic acid alfyl (14) ester are heated for 45 minutes in a vacuum of 10 mm Hg to 100°C, whilst withdrawing the water of reaction produced. After filtration, a light yellow liquid is obtained as the reaction product.

Found % Sn 10.1 (calculated 9.8)

Found % S 8.0 (calculated 7.8)

Example 2:

Manufacture of octyl-tin tris-(cetyl-thioglycollate) containing some dioctyl tin compound.

35.4 g of a mixture of 91% of mono-octyl-tin oxide and 9% of dioctyl-tin oxide, and 121 g of thioglycollic acid cetyl ester are heated for 45 minutes in a vacuum of 10 mm. Hg to 100°C, whilst withdrawing the water of reaction produced. After filtration, a colourless oily liquid is obtained as the reaction product.

Found % Sn 9.6 (calculated 10.2)

Found % S 7.8 (calculated 8.1)

B) Use examples

Example 3:

Heat stability test

A dry blend, consisting of 100 parts of suspension PVC, 0.5 part of montan wax, 1.0 part of monoglycerol ester and 1.0 part of organo-tin stabiliser of Example 2, is milled on a laboratory mill at 190°C. Every 5 minutes, an 0.3 mm thick piece of film is taken off to assist the discolouration. The time in minutes after which the milled film shows a recognisable colour change to light brown-yellow is quoted as a measure of the heat stability and this time was 25 minutes.

The moulding material according to the invention accordingly has a very good heat stability.

Example 4:

A moulding material consisting of 100 parts of bulk-polymerised PVC and 0.3 part of montan wax together with the organo-tin stabiliser of Example 1 is examined for heat stability, analogously to Example 3. The amount of stabiliser is calculated to correspond to the use of 0.15 g of Sn/100 g of PVC.

The time for which the film remained colourless was 35 minutes. A repetition of

the experiment with suspension PVC gives the same result.

Example 5:

100 parts of a vinyl chloride/vinyl acetate copolymer (vinyl acetate content 10%, K-value 60 to 61) are premixed with 0.5 part of montan wax, 1.0 part of monoglycerol ester and an organo-tin stabiliser of the formula



The amount of organo-tin stabiliser (1.35 g) is so chosen that 0.13 g of tin are present per 100 parts of copolymer. After milling for 20 minutes at 180°C, only very slight yellowing is detectable.

Example 6:

A mixture of 100 parts by weight of suspension PVC (K-value 71), 40 parts by weight of di-2-ethylhexyl phthalate, 0.3 part by weight of montan wax and 0.5 part by weight of octyl-tin tris-cetyl-thioglycollate, corresponding to 0.05 g of Sn/100 g of PVC, is milled on a laboratory mill at 180°C until yellowing begins to occur.

The time for which the mixture is milled until a very slight yellowing is just detectable is 74 minutes. After 105 minutes, the mill hide is slightly yellow.

WHAT WE CLAIM IS:—

1. A compound of the formula I



wherein R' represents an alkyl radical containing 12 to 16 carbon atoms.

2. A compound as claimed in Claim 1 in which R' in the formula I represents an alkyl radical with 12 to 14 carbon atoms.

3. A compound as claimed in Claim 1 or Claim 2 in which R' represents the tetradecyl radical.

4. n - Octyl - tin tris - (n - tetradecyl - thioglycollate) of the formula



5. n - Octyl - tin tris(n - dodecyl - thioglycollate) of the formula



6. A process for producing a compound of the formula I defined in Claim 1, which comprises reacting the corresponding octyl stannonic acid or mono-octyl-tin oxide with the appropriate mercapto-acetic acid ester.

7. A process for producing a compound of the formula I, defined in Claim 1, which comprises reacting the corresponding octyl-tin trichloride with the appropriate mercapto-



9

The examples which follow explain the invention in more detail. The percentages given therein are % by weight.

the experiment with suspension PVC gives the same result.

A) Manufacture of compounds of formula I

Example 1:

Manufacture of octyl-tin tris-(alfyl(14)-thioglycollate) containing some dioctyl-tin compound.

14.9 g of a mixture of 91% of octyl-tin oxide and 9% of dioctyl-tin oxide, and 50.0 g of thioglycollic acid alfyl (14) ester are heated for 45 minutes in a vacuum of 10 mm Hg to 100°C, whilst withdrawing the water of reaction produced. After filtration, a light yellow liquid is obtained as the reaction product.

Found % Sn 10.1 (calculated 9.8)

Found % S 8.0 (calculated 7.8)

Example 2:

Manufacture of octyl-tin tris-(cetyl-thioglycollate) containing some dioctyl tin compound.

35.4 g of a mixture of 91% of mono-octyl-tin oxide and 9% of dioctyl-tin oxide, and 121 g of thioglycollic acid cetyl ester are heated for 45 minutes in a vacuum of 10 mm. Hg to 100°C, whilst withdrawing the water of reaction produced. After filtration, a colourless oily liquid is obtained as the reaction product.

Found % Sn 9.6 (calculated 10.2)

Found % S 7.8 (calculated 8.1)

B) Use examples

Example 3:

Heat stability test

A dry blend, consisting of 100 parts of suspension PVC, 0.5 part of montan wax, 1.0 part of monoglycerol ester and 1.0 part of organo-tin stabiliser of Example 2, is milled on a laboratory mill at 190°C. Every 5 minutes, an 0.3 mm thick piece of film is taken off to assist the discolouration. The time in minutes after which the milled film shows a recognisable colour change to light brown-yellow is quoted as a measure of the heat stability and this time was 25 minutes.

The moulding material according to the invention accordingly has a very good heat stability.

Example 4:

A moulding material consisting of 100 parts of bulk-polymerised PVC and 0.3 part of montan wax together with the organo-tin stabiliser of Example 1 is examined for heat stability, analogously to Example 3. The amount of stabiliser is calculated to correspond to the use of 0.15 g of Sn/100 g of PVC.

The time for which the film remained colourless was 35 minutes. A repetition of

Example 5:

100 parts of a vinyl chloride/vinyl acetate copolymer (vinyl acetate content 10%, K-value 60 to 61) are premixed with 0.5 part of montan wax, 1.0 part of monoglycerol ester and an organo-tin stabiliser of the formula



The amount of organo-tin stabiliser (1.35 g) is so chosen that 0.13 g of tin are present per 100 parts of copolymer. After milling for 20 minutes at 180°C, only very slight yellowing is detectable.

Example 6:

A mixture of 100 parts by weight of suspension PVC (K-value 71), 40 parts by weight of di-2-ethylhexyl phthalate, 0.3 part by weight of montan wax and 0.5 part by weight of octyl-tin tris-cetyl-thioglycollate, corresponding to 0.05 g of Sn/100 g of PVC, is milled on a laboratory mill at 180°C until yellowing begins to occur.

The time for which the mixture is milled until a very slight yellowing is just detectable is 74 minutes. After 105 minutes, the mill hide is slightly yellow.

WHAT WE CLAIM IS:—

1. A compound of the formula I



wherein R' represents an alkyl radical containing 12 to 16 carbon atoms.

2. A compound as claimed in Claim 1 in which R' in the formula I represents an alkyl radical with 12 to 14 carbon atoms.

3. A compound as claimed in Claim 1 or Claim 2 in which R' represents the tetradecyl radical.

4. n - Octyl - tin tris - (n - tetradecyl - thioglycollate) of the formula



5. n - Octyl - tin tris(n - dodecyl - thioglycollate) of the formula



6. A process for producing a compound of the formula I defined in Claim 1, which comprises reacting the corresponding octyl stannonic acid or mono-octyl-tin oxide with the appropriate mercapto-acetic acid ester.

7. A process for producing a compound of the formula I, defined in Claim 1, which comprises reacting the corresponding octyl-tin trichloride with the appropriate mercapto-

acetic acid ester in the presence of an HCl acceptor.

8. A compound of the formula I, defined in Claim 1 substantially as hereinbefore described with reference to either Example 1 or Example 2.

9. A process as claimed in Claim 6, substantially as hereinbefore described with reference to Example 1 or Example 2.

10. A thermoplastic moulding material comprising a vinyl chloride polymer or copolymer containing per 100 parts by weight of polymer or copolymer as stabiliser, 0.2 to 5 parts by weight of a compound of the formula I as claimed in Claim 1 or a mixture of two or more of such compounds.

11. Moulding material as claimed in Claim 10 wherein in the compound of the formula I is as claimed in any of claims 2 to 5.

12. Moulding material as claimed in Claim 10 or Claim 11 in which the polymer is a suspension polymer or copolymer, bulk polymer or copolymer or emulsion polymer or copolymer of low emulsifier content.

13. Moulding material as claimed in any of claims 10 to 12 which contains 0.5 to 2 parts by weight of a compound of the formula I.

14. Moulding material as claimed in any of claims 10 to 13 which also contains the dialkyl-tin compound corresponding to the monoalkyl compound of formula I, in an

amount less than, or equal to, that of the monoalkyl compound.

15. Moulding material as claimed in claim 14 in which the dialkyl-tin compound is present in amounts of up to 50 per cent by weight of that of the monoalkyl compound.

16. Moulding material as claimed in any of claims 10 to 15 which also contains other metal stabilisers and/or additives in amount less than, or equal to, that of the monoalkyl tin compound.

17. Moulding material as claimed in claim 16, in which the additional metal stabilisers present are based on organo-tin and are present in amounts of up to 50 per cent by weight relative to the amount of the compound of the formula I.

18. Moulding material as claimed in claim 10, substantially as hereinbefore described with reference to any of Examples 3 to 6.

19. A method of preparing a moulding material as claimed in any of claims 10 to 18 which comprises incorporating the stabiliser into the polymer or copolymer before moulding.

T. SHARMAN,
Agent for the Applicants,
Ciba-Geigy (UK) Limited,
Simonsway,
Manchester, M22 5LB.

