

PATENT SPECIFICATION

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(54) METHOD OF MANUFACTURING A CONCENTRATE OF FIRE-RETARDING FOAM-FORMING SOLID ADDITION SUBSTANCES

(71) We, CALTOP, S.A., a Spanish company of Calle Balmes, 454 Sobreactico, Barcelona, Spain, 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 a method of producing a finely granular concentrate of fire-retarding, foam-forming solid addition agents for host materials such as plastics, varnishes, paints, coating compositions and similar substances. Possible host materials which are comprehended in these terms include thermoplastic and thermosetting plastics moulding or coating compositions, and aqueous dispersion paints.

The invention furthermore concerns the use of the resultant finely granular concentrates as fireproofing agents, particularly in thermoplastic or thermosetting plastic moldings or coating compositions, including aqueous dispersion paints.

It is already known to incorporate in plastics or coating compositions consisting essentially of plastics, addition agents which, under pyrolytic conditions, split off nitrogen and/or water and/or form foam-like carbon structures by which the thermal conductivity is greatly reduced and the flame-retarding action of such additives is thus increased. As such additives, there are known, for instance, solid polyols such as pentaerythritol, nitrogen-containing compounds such as melamine, guanidine, and urea, and also, particularly as foam-formers, ammonium phosphates and polyphosphates.

When using such substances in fire-retarding paints which ordinarily have a thickness of the coating agent of 0.2 to 0.7 mm, foam structures of a height of 5 to 10 mm are formed under conditions of pyrolytic decomposition. The degree of fireproofing in accordance with DIN 4102 corresponds on the average only to approximately classes

F15 to F30, which is due not only to the relatively low height of foam but also to an irregular foam structure and poor mechanical strength, which results from the need for relatively high content of substances of fire-retarding or foaming action and their frequently insufficient compatibility with the plastic binders (due for instance to hydrophilic properties of the polyols). Furthermore, said paints or coating compositions are of poor resistance to the elements, for the same reasons.

It has been found that these disadvantages may be ameliorated or avoided if the fire-retarding additions are brought into a specific form of a finely granular concentrate which is compatible with the binder and assures a uniform distribution of the active substance upon introduction into the binder or plastics material.

The method in accordance with the invention for the production of a finely granular concentrate of fire-retarding foam-forming solid addition substances for plastics, paints, coating compositions or similar host substances comprises reducing the additives to a particle size of less than 5 μm ;

subsequently coating said additives with a polymeric binder material;

drying the coated additives at a temperature of not more than 200°C; and

crushing the dried and coated additives to give a granular product having a particle size of not more than 50 μm .

After the coating step, the additives are generally no longer in the form of particles of less than 5 μm .

The coated additives may be rolled into sheet form prior to the drying step. Preferably the coating, drying and crushing steps are repeated on said granular product, using the same or different polymeric binder material(s).

The polymeric binder is desirably one which will show good compatibility with the host substance into which the concentrate is

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to be introduced. For example, the host and the binder may be the same material.

5 Preferably the concentrates should contain 30 to 90% by weight of the fire-retarding additives.

10 The production of granules of a coated concentrate from the fire-retarding additives can prevent the premature separating out of such additives, which was a general problem in the prior art as a result of different densities, and it thus can assure the development of a uniform foam layer and thus of fire protection which is highly uniform at all places.

15 In accordance with one embodiment of the invention, the following procedure is employed.

The individual addition substances, including the foam-forming agents, are subjected to a milling for 12 to 24 hours, the size of the individual particles produced being less than 5 μ m and preferably less than 1 μ m. After the milling the particles are coated with a known polymeric binder, such as a paint or plastics material and allowed to pass through a roll mill. The mass is then dried in a very thin layer, preferably under reduced pressure. The drying temperature is not greater than 200°C and should preferably be 100°C.

30 After full dryness is reached, the mass is again subjected to a grinding process. The degree of fineness depends in this connection on the purpose of use. In the case of coating compositions which are to be applied in a thick layer, the powder produced by the grinding process can have a particle size of 5 to 10 μ m on the average, and at most 50 μ m. In this case, little serious damage to the surface of the materials occurs and the individual components of the active mixture are surrounded by a protective covering. When mixed into the coating material (the last substance), the surrounded active particles of the fire-retarding addition substances remain at a predetermined distance apart and highly active.

45 Upon an increase in temperature above 500°C, the fire-retarding reactions take place substantially more rapidly and the conduction of heat is reduced already at a very early time. A considerable increase in fire resistance is obtained hereby as compared with normal mixing. Thus, coating compositions which were just suitable for the obtaining of fire protection class F30 can be placed in class F60.

55 It may be possible for these values to be further increased if the material obtained after the first coating procedure is subjected to a second or third treatment.

60 In a preferred form of the invention, in order to increase the effectiveness of the concentrate, at least in the last outer layer there is used a polymeric material which splits off nitrogen and/or water under pyrolytic conditions. Epoxy resins, melamine resins, or unsaturated hydroxy-group containing polyesters which have been hardened by amines and/or

amides are particularly suitable, and therefore preferred, polymeric substances for this purpose.

The application of the coating is effected in known manner, e.g. by dipping, impregnating and stirring. In many cases, counter-current spraying is preferred since it provides a particularly uniformly coated powder. Fluidized-bed methods can in certain cases also give favorable results.

70 It is furthermore preferred to use, for at least one layer of the coating of the flame-retarding addition substances, a polymeric material which reacts endothermally with the host substance or at least another layer of the binder under pyrolytic conditions. There are suitable for this purpose, for instance, condensation resins of phenols with nitrogen compounds, for instance polyalkyl ureas, such as compounds of p-cresol with dimethyl urea or else α -ureido alkylation products of phenols.

As fire-retarding addition substances for the method of the invention, there enter into consideration most substances known for this purpose, such as phosphorus compounds, polyols, amines, and/or amides. In addition, water-binding mineral substances can also be used, such as the minerals known as "molecular sieves" (zeolites), $Al(OH)_3$, and hemihydrate. The fire-retarding phosphorus compounds tri-p-cresylphosphate, phosphorous chloride acid phenyl esters, ammonium dihydrogen phosphate, trisodiumphosphate hydrate, disodiumphenylphosphate and/or colamine phenolphthaleinphosphate are substances which are particularly well suited for the method of the invention.

The finely granular concentrates prepared in accordance with the invention can be used as fire-retarding foam-forming addition substances in thermoplastic or thermosetting plastic molding or coating compositions, including aqueous dispersion paints.

100 The powders serve, for instance, for incorporation in epoxy resin compositions which are to be worked further to form flame-protected plates or sandwich structures or else tubes, particularly in petrochemistry, for instance, for refineries. Such mixtures can be employed also as gel coats, for instance, on additional resin substrates or other substrates such as wood, chipboard, or cardboard. Together with the powders described in accordance with the invention, there can readily be used additional flame-retarding substances or substances which form insulation layers, interaction between the different additives being substantially reduced by the use of the coated concentrates of the invention as compared with what was previously the case.

125 Concentrate powders prepared in accordance with the invention can also be used in aqueous dispersion. This includes also phenol-resin dispersions which serve for the re-

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inforcing of glass fibers and can produce a considerable amount of heat insulation in case of fire. In addition to this, it is no longer necessary to limit the amount of such dis-
 5 persions used per cubic meter to a minimum, but the amount can depend on the technical requirements. By varying the composition of the powder centre and the surrounding outer skin, the powder can be excellently adapted to
 10 the specific purpose of use and, in addition, to the base material, which was not possible in accordance with the prior art.

The invention will be further explained by the following examples.

Example 1

The following substances are subjected to a grinding process for 12 hours to reduce them to a particle size of less than $5\mu\text{m}$:

100 g ammonium dihydrogenphosphate
 50 g pentaerythritol
 30 g melamine formaldehyde resin (cured in powder form)
 5 g phosphorus chloride acid phenyl ester

After the grinding, the products are introduced into a 50% by weight solution of chlorinated rubber in benzene and dried in vacuum. The dried components are again ground in a ball mill to a powder having a portion of particles of a size of at most $50\mu\text{m}$.
 30 The maximum point of the distribution curve was at $10\mu\text{m}$.

The powder was mixed in an amount of 30% by weight with a p-cresol dimethylurea condensate, dried at about 150°C , again ground, again mixed with the condensate, dried and ground, and then mixed into an alkyl enamel. Coating wood with this, dispersion paint gave, upon the fireproofing test in accordance with DIN 4102, a fire protection class of F50. In contradistinction to this, with the same enamel which contained the same flame protective additions in the same quantity, but not coated in accordance with the invention, a fire protection class of only F30 was obtained.

Example 2

The following substances were ground for 24 hours in a ball mill to reduce them to a particle size of less than $5\mu\text{m}$:

150 g of monoammonium phosphate
 50 g of pentaerythritol
 40 g of diethylene tetramine
 20 g of a chlorinated paraffin
 10 g of zeolite

The mass was thereupon introduced into an epoxy resin aminoamide hardener mixture having a viscosity of 500 cP and cured. 150 g of epoxy resin were used and the amount of hardener adapted to the epoxy number and amine equivalent was employed. The epoxy

resin was an adduct of epichlorhydrin and bisphenol A.

After the curing, the mixture was subjected to a further fine grinding process and ground down to an average particle size of $5\mu\text{m}$.

Thereupon, the material was sprayed in countercurrent with a solution of an epoxy resin anhydride mixture in a ratio of 1 : 1 and dried and hardened during its fall through a spray tower with a temperature of 130°C . In this way, there was produced a second outer skin around the dry concentrate powder, only a slight amount of grinding being necessary after the curing in order to separate from each other any particles which might be adhering together so that the particle size is not greater than $50\mu\text{m}$.

Thereupon the powder was wind-screened in order to obtain a uniform fineness.

The powder in an amount of 35% by weight was worked together with a similar epoxy resin hardener mixture to form glass fiber reinforced tubes. The tubes exhibited fire protection of class F60 in accordance with DIN 4102.

WHAT WE CLAIM IS:—

1. Method of producing a finely granular concentrate of fire-retarding foam-forming solid additives for plastics, paints, coating compositions or similar host substances, which comprises:

reducing the additives to a particle size of less than $5\mu\text{m}$;

subsequently coating said additives with a polymeric binder material;

drying the coated additives at a temperature not more than 200°C ; and

crushing the dried and coated additives to give a granular product having a particle size of not more than $50\mu\text{m}$.

2. Method according to claim 1 wherein the coated additives are rolled to form a rolled sheet prior to the drying step.

3. Method according to claim 1 or claim 2 wherein the coating, drying and crushing steps are repeated on said granular product, using the same or different polymeric binder material(s).

4. Method according to any one of the preceding claims wherein said polymeric binder material comprises a plastics resin material and/or is compatible with such resin materials.

5. Method according to any one of the preceding claims wherein the amount of the additives is so selected that they constitute 30 to 90% by weight of the final concentrate.

6. Method according to any one of the preceding claims wherein the polymeric binder material used in said coating step, or in at least the last coating step when there is a plurality thereof, is a material which splits off nitrogen and/or water under pyrolytic conditions.

7. Method according to claim 6 wherein

- said polymeric binder material which splits off nitrogen and/or water comprises an epoxy resin which is hardened by amines and/or amides, a melamine resin, or an unsaturated polyester containing hydroxyl groups. 35
- 5 8. Method according to any one of the preceding claims wherein the or a said coating step is effected by countercurrent spraying. 40
- 10 9. Method according to any one of the preceding claims wherein the or a said polymeric binder material comprises a material which reacts endothermically under pyrolytic conditions with plastics resin materials. 45
- 15 10. Method according to any one of the preceding claims wherein said additives are or include phosphorous compounds and/or polyols and/or amines and/or amides. 50
- 20 11. Method according to claim 10 wherein said additives include mineral substances having bound water. 55
- 25 12. Method according to claim 10 or 11 wherein said additives include tri-p-cresyl-phosphate and/or phosphorus chloride acid-phenylester and/or ammonium dihydrogen phosphate and/or trisodium phosphate hydrate and/or disodium phenylphosphate and/or colamine phenolphthalein phosphate. 60
- 30 13. A method of producing a concentrate substantially as herein described in Example 1 or Example 2.
14. A concentrate of fire-retarding foam-forming solid addition substance produced by the method of any one of the preceding claims.
15. A method of producing a composition (such as a plastics material, paint or coating composition) comprising a fire-retarding concentrate and a host material said method comprising:
- producing said concentrate according to the method of any one of claims 1 to 13 wherein said polymeric binder material used in said coating step, or in at least the last coating step when there is a plurality thereof, is identical to and/or compatible with said host material; and
- processing said concentrate and said host material or precursor(s) thereof to produce said composition.
16. A method according to claim 15 wherein the or a said polymeric binder material comprises a material which reacts endothermically with the host material under pyrolytic conditions.
17. A concentrate of foam-forming solid addition substances substantially as herein described with reference to Example 1 or Example 2.
18. A thermoplastic or thermosetting plastic molding or coating composition incorporating a concentrate according to claim 16 or claim 17.
19. The product of the method of claim 15.

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