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(54) PHENOL-FORMALDEHYDE FOAMS AND NOVOLAK RESIN COMPOSITIONS FOR USE IN THE PREPARATION THEREOF

(71) We, SOCIETE CHIMIQUE DES CHARBONNAGES, of Tour Aurore-Cedex 5, 92080 Paris la Defense, France, a body corporate organised under the laws of France, 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 process for the simultaneous manufacture and application of phenol-formaldehyde foams, the manufacture comprising mixing two fluids and the application comprising injecting or projecting the foam formed by the mixing.

Apparatus essentially comprising storage tanks, which may be heated, feed pumps, appropriate piping, which may be heated and a mixing head have been proposed for the manufacture and application of urea-formaldehyde or polyurethane foams. It has appeared to be desirable to use apparatus of this type for the manufacture and application of phenol-formaldehyde type foams; for this, it is essential to have two constituents available, which may be separately stored and separately pumped, but which, by introduction into the mixing head of the above-mentioned apparatus, lead to a mixture which is transformed into a homogeneous and high-quality foam in the places where the mixture is injected or projected.

It is also desirable, in the preparation of these phenol-formaldehyde foams, to use constituents which give the foams good mechanical properties (a lesser tendency to fissuring and friability) and a better resistance to heat.

We have found according to the present invention that, in order to achieve the above-mentioned aims, it was firstly desirable to use a new Novolak composition, in the form of an anhydrous solution and comprising:

(a) from 19 to 23%, by weight, of methylene chloride;
(b) from 10 to 20%, by weight, of phenol-sulphonic acid; and
(c) from 60 to 70%, by weight, of at least one Novolak resin obtained by the polycondensation, with the aid of an acid catalyst, of a mixture of phenol and formaldehyde in a molar ratio within the range of from 1:0.6 to 1:0.5, inclusive.

In addition, it is very desirable to use a homogeneous Resole phase having a viscosity within the range of from 200 to 250 poises, inclusive, at 20°C., and containing from 75 to 95%, by weight, of at least one Resole resin obtained by polycondensation with the aid of a basic catalyst, of a mixture of phenol and formaldehyde in a molar ratio within the range of from 1:2 to 1:2.5, inclusive, and of 5 to 25%, by weight, of water.

Both of the two phases which can be used to carry out the invention may contain a surface-active agent which, as known in the phenol-formaldehyde foam manufacturing industry, acts on the uniformity of the cells which are formed.

The foam may be prepared by mixing the two phases defined above and projecting the mixture thus formed into the place where the foam is formed by natural and spontaneous evolution of the mixture. The relative quantities of the two phases are practically identical, that is to say, for example, that each phase must represent from 45 to 55% of the mixture; the fact that the best phenol-formaldehyde foams obtained in the process according to the invention are those for which a final phenol-formaldehyde molar ratio of substantially 1.5:1 is obtained, is preferably taken into consideration.

The temperature at which the mixture of the two phases takes place is important with

regard to the properties of the finished product; we have found according to the present invention that the said temperature must be within the range of from 15 to 65°C., inclusive. Besides, it is not necessary for the two phases to be brought to the same temperature when they are mixed; on the contrary, we have found that it is often desirable for the temperature of the Novolak phase (phase containing the catalyst) to be some degrees higher than the temperature of the Resole phase.

The time for which the mixture remains (in the interior of the mixing head) can vary from approximately 5 seconds to approximately 1 minute, 30 seconds; of course, it depends on the reagents themselves and on the temperature at which the mixture is formed. It is usually desirable to regulate the time during which the mixture remains in the "mixing head" in such a way that the expansion phenomenon of the foam develops as soon as the mixture leaves the "head".

The non-limiting Examples below illustrate the invention. The percentages are by weight.

EXAMPLE 1.

a) Preparation of the Resole and the Resole phase.

4,700 g phenol and 7,654 g of 49% aqueous formaldehyde solution are placed in a reactor. The molar ratio of phenol to formaldehyde is 1:2.5. The mixture is heated to boiling and 208 g of 48% caustic soda lye are gradually introduced, the total amount of caustic soda lye being introduced within 15 minutes. Heating takes place for 20 minutes and then, after cooling, the mixture is neutralized with the aid of acetic acid until a pH value of 7 is obtained (202 g of 50% aqueous acetic acid were used for this purpose).

The Resole obtained is dried until a product having a Brookfield viscosity within the range of from 200 to 220 poises at 20°C. is obtained.

We have noted that, under these conditions, a Resole having a "water content" of 24.3% can be obtained. This content is evaluated by means of the following test:

4 g of the Resole are introduced into a dish which is placed in a ventilated oven heated to 140°C; the duration of the test is 3 hours; by weighing before and after the test, the weight difference of the sample is determined, and this is the difference which is called the "water content" of the tested product.

The Resole obtained is stable and storable. It is used after the addition of approximately 2% Cemulsol B, for example (Cemulsol B being an emulsifier formed from polyoxyethylenised castor oil).

b) Preparation of the Novolak and of the Novolak phase.

5,640 g phenol and 2,204 g of 49% aqueous formaldehyde solution are placed in a reactor. The molar ratio of phenol to formaldehyde is 1:0.6. The mixture is heated to boiling and a total quantity of 117.6 g of 10% aqueous sulphuric acid is gradually added for 20 minutes. Boiling is maintained for 30 minutes. The mixture is then cooled. 1,646 g of a mixture of phenolsulphonic acid and ethanol are added to the mixture in relative proportions, by weight, of 100/20. The mixture is then dried under a vacuum until the water is totally eliminated, this elimination being carried out by azeotropic distillation with the aid of the excess phenol present which is recycled in the reactor after condensation and decantation of the azeotrope. Some methylene chloride (1,826 g) is then added to the Novolak which has been prepared in this way and 1%, by weight, of Cemulsol B in relation to the overall mixture. A homogeneous, stable mixture is thus obtained which has a Brookfield viscosity of substantially 65 poises at 30°C.

c) Mixture and preparation of the foam.

The Resole phase and the Novolak phase are pumped at a temperature of substantially 30°C. and mixed in a mixing head. The relative proportions of the two solutions are approximately 50/50, by weight. The time for which the mixture remains in the mixing head is of the order of 20 seconds. The mixture is projected into a vessel where it immediately begins to expand. The maximum temperature attained by the mixture in reaction is approximately 87°C. The total expansion lasts approximately 1 minute 15 seconds. A foam is thus obtained having cells of dimensions within the range of from 0.2 to 1 mm, inclusive (average diameter), which are distributed fairly regularly between the centre and the periphery of the sample.

EXAMPLE 2.

The same Resole resin and the same Novolak resin as in Example 1 are used but the quantities of phenolsulphonic acid and of methylene chloride added to the Novolak resin are increased. A foam whose pores have an average diameter of 0.1 to 0.5 mm is obtained with a 1,980 g quantity of dry phenolsulphonic acid and a quantity of 1,980 g methylene chloride, spending only 5 seconds in the mixing head.

EXAMPLE 3.

The following tests were carried out, starting from Resoles prepared according to the general process described under part (a) above of Example 1, using the reagents (phenol, formaldehyde, caustic soda) in a molar ratio of 1/2/0.05. By altering the boiling time and the degree of dryness under vacuum Resole having the respective Brook-

field viscosities at 20°C shown below, and water contents of 20 to 25% by weight, were obtained:

200 Poises	(R_{200})
210 Poises	(R_{210})
240 Poises	(R_{240})

Novolaks were prepared separately according to the general process described under part (b) above of Example 1 by using the reagents (phenol, formaldehyde, sulphuric acid) in the following molar ratios:

1/0.5/0.001	(C_1)
1/0.6/0.002	(C_2)
1/0.5/0.002	(C_3)

With the aid of these Resolves and of these Novolaks, the Resole and Novolak phases were prepared:

A Resole phases: one part by weight of Cemulsol B (emulsifier formed from a polyoxyethylenised castor oil) for 49 parts by weight of Resole.

B Novolak phases: various quantities (expressed in parts by weight) of phenolmonosulphonic acid, methylene chloride, and 1% by weight in relation to the mixture of Cemulsol B were added to each of the Novolaks.

The Resole and Novolak phases previously prepared were then mixed as in Example 1. The temperature of the two phases at the moment of mixing was still 30°C.; the time which the two phases spent in the mixing head varied from 15 to 30 seconds; the relative quantities, by weight, of the Resole phase and the Novolak phase were maintained at 50/50.

The results obtained are shown in the following table.

TABLE

Resole phase used (Resole: 49 parts Cemulsol B: 1 part)	Novolak phase (contains in addition and in each case 0.5 part of Cemulsol B).			Duration (seconds)	Maximum temperature for expansion (°C)	Foam obtained		
	Novolak (nature, part by weight)	Phenolsulphonic acid (part by weight).	CH_2Cl_2 (part by weight)			average diameter of cells (mm)	density g/l	
							average	at core
R_{200}	C_1; 34	6	10	20	89	0.4–2	37	16
R_{200}	C_1; 33	7	10	15	90	0.4–2	41	16
R_{200}	C_2; 34	6	10	15	90	0.2–1	48	17
R_{200}	C_2; 35	5	10	30	90	0.3–1.5	48	20
R_{200}	C_2; 33.5	5	11.5	30	85	0.3–1.5	56	18
R_{210}	C_1; 31	9	10	30	90	0.2–1	48	27
R_{240}	C_1; 34	6	10	15	88	0.3–1.5	28	15
R_{240}	C_3; 34	6	10	20	88	0.3–1.5	39	17

WHAT WE CLAIM IS:—

1. A composition comprising a Novolak resin for use in the preparation of phenol-formaldehyde foam, which comprises an anhydrous solution containing:

(a) from 19 to 23%, by weight, of methylene chloride;
(b) from 10 to 20%, by weight, of phenol-sulphonic acid; and
(c) from 60 to 70%, by weight, of at least one Novolak resin obtained by polycondensation, with the aid of an acid catalyst, of a mixture of phenol and formaldehyde in a molar ratio within the range of from 1:0.6 to 1:0.5, inclusive.

2. A process for the preparation of a phenol-formaldehyde foam, in which (i) the following components (A) and (B) are introduced into a mixer, namely:

(A) a homogeneous Resole phase having a viscosity within the range of from 200 to 250 poises, inclusive, at 20°C., and containing from 5 to 25%, by weight, of water and from 75 to 95%, by weight, of at least one Resole resin obtained by polycondensation, with the

aid of a basic catalyst, of a mixture of phenol and formaldehyde in a molar ratio within the range of from 1:2 to 1:2.5, inclusive; and

(B) an anhydrous homogeneous Novolak phase containing:

(a) from 19 to 23%, by weight, of methylene chloride;

(b) from 10 to 20%, by weight, of phenol-sulphonic acid; and

(c) from 60 to 70%, by weight, of at least one Novolak resin obtained by polycondensation,

with the aid of an acid catalyst, of a mixture of phenol and formaldehyde, in a molar ratio within the range of from 1:0.6 to 1:0.5, inclusive, the relative weights of components (A) and (B) being substantially the same, and the components (A) and (B) being mixed at a temperature of from 15 to 65°C and remaining within the mixer for a period of time within the range of from 5 to 90 seconds, inclusive, and (ii) the resulting mixture is projected outside the mixer to give the desired foam spontaneously.

3. A process according to claim 2, in which the components (A) and (B) are brought to the mixer by pumping, at a temperature within the range of from 15°C. to 65°C., inclusive.

4. A process for the preparation of a phenol-formaldehyde foam as claimed in Claim 2, substantially as herein described with reference to any of the specific Examples.

5. A phenol-formaldehyde foam produced by a process as claimed in any of claims 2 to 4.

6. A composition comprising a Novolak resin for use in the preparation of a phenol-formaldehyde foam as claimed in Claim 1, substantially as herein described with reference to any of the specific Examples.

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