Patented Oct. 7, 1952

2,613,189

UNITED STATES PATENT OFFICE

2,613,189

CELLULAR MATERIAL AND BLOWING AGENT THEREFOR

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No Drawing. Application September 2, 1950, Serial No. 183,100

19 Claims. (Cl. 260—2.5)

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This invention relates to a cellular material such as a cellular rubber composition and pertains more specifically to a blowing agent and a method of using the same in the manufacture of vulcanized sponge rubber.

The object of this invention is to provide a blowing agent which is more effective than those hitherto known and which produces a product having superior properties.

Another object is to provide a method of making a cellular material from a plastic composition which material is characterized by having a soft texture and by having cells of uniform size which are for the most part interconnected.

Two general types of synthetic cellular material are well known, one in which the individual cells are discrete chambers separated from each other by a wall of material, the other in which the individual cells are interconnected to provide a product which is pervious to fluids. In making products of the latter type, two general methods have been employed, the first of which involves beating or whipping air into a liquid dispersion or solution of the binder material to form a froth or foam, then gelling or setting the foam; the second involves dispersing in the solid binder material an ingredient which will liberate gas upon heating to form bubbles or cells. In this latter method, finely-divided sodium bicarbonate has been one of the principal blowing agents employed up until the present time. This ingredient reacts to liberate carbon dioxide upon subsequent heating of the composition. If desired, acidic materials may be present, such as the cottonseed fatty acids commonly employed in rubber compounding in order to accelerate liberation of the gas.

However, the results obtainable with sodium bicarbonate have not been entirely satisfactory in that even by using a large proportion of this ingredient it has been impossible to reduce the apparent density of the finished product to the desired point. Furthermore, the cells in the finished product are larger than is desired for many purposes and are not uniform in size but vary over a wide range. Consequently the products tend to be stiff and boardy and of varying compressibility.

I have now discovered that by adding to sodium bicarbonate a small amount of an amide having the formula $(CH_2N_2)_x$ where x is a small integer, these disadvantages are overcome and a highly desirable product is obtained. This result apparently is due to a synergistic effect between these two ingredients since the amide by

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itself produces only a small degree of blow, much less than that of an equal amount of sodium bicarbonate. The amides which I have found to be particularly effective are cyanamide, dicyandiamide and melamine, of which melamine is preferred because of the superior results which it produces. A mixture of sodium bicarbonate and amide containing from 2 to 30% by weight of amide is satisfactory although from 3 to 10% is preferred, the best results being obtained by the use of about 5% of amide by weight of the mixture.

It has been found desirable and convenient to mix the sodium bicarbonate and amide in finely-divided form prior to incorporating the mixture in the material to be blown. However, if desired, the two ingredients may be separately dispersed in the material to be blown. The precise particle size of the bicarbonate and of the amide is not critical. I have found commercial baking soda to be quite satisfactory, and the particle size of the amide is preferably of the same order of magnitude as that of the bicarbonate. Material which will pass a No. 50 U. S. Standard sieve is satisfactory, although it is preferred to use material which is fine enough to pass a No. 100 U. S. Standard sieve.

The amount of this new blowing agent which should be used will vary, of course, depending upon the plasticity of the uncured composition and the apparent density desired in the finished product. Satisfactory results have been obtained by using from 2 to 30% of the blowing agent by weight of the binder material such as rubber. However, it is preferred in most cases to employ from 3 to 10% by weight.

My new blowing agent may be used with any heat-softening or thermoplastic binder material which is capable of being blown to a cellular product by means of sodium bicarbonate alone, regardless of whether the material is hardened or set in its cellular condition merely by cooling or by a chemical reaction such as vulcanization. Among such binder materials are phenol aldehyde resins, urea formaldehyde resins, melamine formaldehyde resins, polyethylene, polyisobutylene, polyvinyl resins such as polyvinyl acetals, plasticized polyvinyl chloride, various copolymers of vinyl chloride with other polymerizable materials, and natural or synthetic rubbers such as caoutchouc (a polymer of isoprene) and various other rubbery conjugated diene polymers such as the rubbery polymers of butadiene-1,3, chloroprene, 2,3-dimethyl butadiene and the like and rubbery copolymers of these materials with each

other and with other copolymerizable ingredients such as styrene, methyl acrylate, methyl methacrylate, vinyl pyridine, chlorostyrene, acrylonitrile, isobutylene and the like. The blowing agent is particularly valuable for use with sulfur-vulcanizable rubbery materials.

As in the case of the use of sodium bicarbonate alone as a blowing agent, it is desirable but not essential that some acidic ingredient be present in the composition to react with the sodium bicarbonate upon heating to liberate a gas and cause cell formation. Preferably this acidic ingredient is an organic acid such as the fatty acids commonly employed in rubber compounding.

The following specific examples are intended as illustrations of my invention but not as a limitation thereon.

Example 1

The following composition was prepared by mixing the ingredients on a roll mill, the sodium bicarbonate being added last:

	Parts by weight
Crude rubber	100.0
Whiting	85.0
Channel black	2.0
Zinc oxide	5.0
Sulfur	3.0
Mineral oil	10.0
Cottonseed fatty acid	20.0
Petrolatum	2.0
Sincera wax	2.0
Accelertor (dibenzothiazyl disulfide)	0.6
Sodium bicarbonate (commercial baking soda)	20.0
Total	249.6

The composition was heated in a mold at 300° F. for 30 minutes to cause cell formation and vulcanization. By using various amounts of this rubber composition it was determined that 100 grams of the composition was required to produce a cellular product completely filling a standard mold (18 cu. in.), the product having an apparent density of .22 oz. per cu. in. When less than 100 g. of the composition was employed, the material failed to fill out the mold completely during the blowing stage.

The product in this case was stiff and boardy and the individual cells varied consideraly in size from about $\frac{1}{32}$'' to about $\frac{1}{4}$'' in diameter. This non-uniformity in size of the cells resulted in the product having varying compressibility at different spots, one area being quite firm while another adjacent area was relatively soft.

Example 2

The sodium bicarbonate in Example 1 was replaced with 5 parts by weight of a mixture of 95 parts by weight of finely-divided sodium bicarbonate (commercial baking soda) with 5 parts by weight of finely-divided melamine and treated in the same manner.

It was found that 40 g. of this composition sufficed to fill the standard mold resulting in a product having an apparent density of .078 g. per cu. in. The product was characterized by a soft texture and very uniform cell size (about $\frac{1}{32}$''), which was considerably smaller than the cell size of the product prepared using sodium bicarbonate alone.

Example 3

The sodium bicarbonate of Example 1 was replaced with 5 parts by weight of a mixture of 70 parts by weight of sodium bicarbonate with 30 parts by weight of melamine. The results obtained were similar to those of Example 2.

Example 4

The sodium bicarbonate of Example 1 was replaced with 5 parts by weight of a mixture of 95 parts by weight of sodium bicarbonate and 5 parts of cyanamide and treated as in Example 1.

In this case it was found that the 5 parts of new blowing agent was approximately equivalent in blowing power to 20 parts of sodium bicarbonate, about 100 g. of the composition being required to fill the standard mold. In addition, the product was similar to that of Examples 2 and 3 in texture and uniformity of cell size.

Example 5

The sodium bicarbonate of Example 1 was replaced with 5 parts by weight of a mixture of 95 parts by weight of sodium bicarbonate with 5 parts of dicyandiamide and treated as in Example 1.

The results in this case were approximately the same as those obtained in Example 4.

Example 6

The sodium bicarbonate of Example 1 was replaced with 10 parts by weight of a mixture of 98 parts by weight of sodium bicarbonate with 2 parts of melamine and treated as in Example 1. The results were similar to those in Example 2.

Similar results were obtained using as little as 2 parts by weight of the new blowing agent per 100 of rubber and as much as 30 parts by weight per hundred of rubber. Best results however were obtained by using from 3 to 10 parts by weight per hundred of rubber.

In the case of each of the products of the foregoing examples, substantially all of the cells were interconnected.

When the new blowing agent is employed with other binder materials such as phenolic resins, polyvinyl resins or the like, the various minor changes in the other ingredients usually present in the composition will be apparent to those skilled in the art. Vulcanizable synthetic rubbers such as butadiene-styrene copolymers, butadiene-isobutylene copolymers, neoprene, and the like, may be used in place of the crude rubber in the recipe given in Example 1, of course, with only the conventional changes in amount and kind of vulcanizing agent, accelerator, plasticizer, etc, as are well known to the art.

Obvious variations and modifications which are within the scope of the appended claims will be apparent to those skilled in the art.

I claim:

1. A blowing agent comprising a mixture of solid, finely-divided sodium bicarbonate with from 2 to 30%, by weight of the mixture, of a solid, finely-divided amide selected from the class consisting of cyanamide, dicyandiamide, and melamine.

2. A blowing agent comprising an intimate mixture in particulate form of sodium bicarbonate with from 3 to 10%, by weight of the mixture, of an amide selected from the class consisting of cyanamide, dicyandiamide, and melamine.

3. A blowing agent comprising solid, finely-divided sodium bicarbonate having uniformly mixed therewith from 3 to 10%, by weight of the mixture, of finely-divided cyanamide.

4. A blowing agent comprising solid, finely-

divided sodium bicarbonate having uniformly mixed therewith from 3 to 10%, by weight of the mixture, of finely-divided dicyandiamide.

5. A blowing agent comprising solid, finely-divided sodium bicarbonate having uniformly mixed therewith from 3 to 10%, by weight of the mixture, of finely-divided melamine.

6. A composition capable of being blown to cellular form comprising a heat-softening binding material having dispersed therein a mixture in finely-divided form, of sodium bicarbonate with from 2 to 30%, by weight of the mixture, of an amide selected from the class consisting of cyanamide, dicyandiamide, and melamine.

7. A composition for making cellular material which comprises a vulcanizable rubbery diene polymer having dispersed therein a particulate mixture comprising sodium bicarbonate and from 3 to 10%, by weight of the mixture, of an amide selected from the class consisting of cyanamide, dicyandiamide, and melamine.

8. A composition for making cellular material comprising a vulcanizable rubber containing dispersed therein from 2 to 30%, by weight of the rubber, of sodium bicarbonate and an amide selected from the class consisting of cyanamide, dicyandiamide, and melamine, said amide amounting to 2 to 30% of the total weight of said bicarbonate and amide.

9. A composition for making cellular material comprising a vulcanizable rubber containing dispersed therein from 2 to 30%, by weight of the rubber, of sodium bicarbonate and cyanamide, said amide amounting to 3 to 10% of the total weight of said bicarbonate and amide.

10. A composition for making cellular material comprising a vulcanizable rubber containing dispersed therein from 2 to 30%, by weight of the rubber, of sodium bicarbonate and dicyandiamide, said amide amounting to 3 to 10% of the total weight of said bicarbonate and amide.

11. A composition for making cellular material comprising a vulcanizable rubber containing dispersed therein from 2 to 30%, by weight of the rubber, of sodium bicarbonate and melamine, said melamine amounting to 3 to 10% of the total weight of said bicarbonate and melamine.

12. The method of making a spongy material which comprises dispersing in a heat-softening composition finely-divided sodium bicarbonate and an amide selected from the class consisting of cyanamide, dicyandiamide, and melamine, said amide amounting to 2 to 30% of the total weight of said bicarbonate and amide, and heating said composition to soften it and to liberate gas from said bicarbonate to form interconnected cells of uniform size dispersed throughout said composition.

13. The method of making a cellular sponge composition which comprises dispersing in a composition comprising a vulcanizable rubbery conjugated diene polymer from 2 to 30%, by weight of said polymer, of sodium bicarbonate and cyanamide, said amide amounting to 3 to 10% of the total weight of said bicarbonate and amide, and heating said composition to soften it and to liberate gas from said bicarbonate to form interconnected cells of uniform size dispersed throughout said composition and to vulcanize said composition.

14. The method of making a cellular sponge composition which comprises dispersing in a composition comprising a vulcanizable rubbery conjugated diene polymer from 2 to 30%, by weight of said polymer, of sodium bicarbonate and dicyandiamide, said amide amounting to 3 to 10% of the total weight of said bicarbonate and amide, and heating said composition to soften it and to liberate gas from said bicarbonate to form interconnected cells of uniform size dispersed throughout said composition and to vulcanize said composition.

15. The method of making a cellular sponge composition which comprises dispersing in a composition comprising a vulcanizable rubbery conjugated diene polymer from 2 to 30%, by weight of said polymer, of sodium bicarbonate and melamine, said melamine amounting to 3 to 10% of the total weight of said bicarbonate and melamine, and heating said composition to soften it and to liberate gas from said bicarbonate to form interconnected cells of uniform size dispersed throughout said composition and to vulcanize said composition.

16. The method of making a cellular sponge composition which comprises dispersing in a composition comprising a vulcanizable rubbery conjugated diene polymer from 3 to 10%, by weight of said polymer, of sodium bicarbonate and melamine, said melamine amounting to about 5% of the total weight of said bicarbonate and melamine, and heating said composition to soften it and to liberate gas from said bicarbonate to form interconnected cells of uniform size dispersed throughout said composition and to vulcanize said composition.

17. A composition for making cellular material which comprises a heat-softening binding material having dispersed therein a mixture in finely-divided form of sodium bicarbonate with from 2 to 30%, by weight of the mixture, of melamine.

18. A composition for making cellular material which comprises a heat-softening binding material having dispersed therein from 3 to 10%, by weight of said binding material, of a mixture in finely-divided form of sodium bicarbonate with from 3 to 10%, by weight of the mixture, of melamine.

19. The method of making a spongy material which comprises dispersing in a heat-softening composition finely-divided sodium bicarbonate and melamine, said melamine amounting to 3 to 10% of the total weight of said bicarbonate and melamine, and heating said composition to soften it and to liberate gas from said bicarbonate to form interconnected cells of uniform size dispersed throughout said composition.

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