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ICE REINFORCEMENT

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This invention relates to a method of reinforcing frozen liquids, and more particularly relates to a method for obtaining homogeneous, frozen liquid compositions containing relatively high concentrations of reinforcing material.

It is known that the compressive and tensile strengths of pure ice are greater than those of many concretes, and that the strength of ice can be appreciably increased by incorporating a finely divided, preferably fibrous, inert material into the liquid before freezing. Such compositions can be used to construct facilities in cold regions such as the Arctic. They can also be employed in the Torrid or Temperate Zones provided there is adequate refrigeration available. For example, such compositions can be employed in the construction of storage containers for liquefied hydrocarbon gases.

The compositions should comprise a substantially homogeneous mixture of liquid and reinforcing material. Moreover, the strength of the frozen composition increases substantially linearly with the increasing volume fraction of fibrous material that is added to the liquid. There are problems associated with the mixing of such compositions which here heretofore made it impossible to obtain substantially homogeneous, bubble free compositions comprising liquid and relatively large amounts of fibrous fillers.

One problem is that the fibrous fillers usually segregate either by sinking or floating in the liquid at a relatively high rate after the filler has been admixed with the liquid. Therefore, by the time the composition has been frozen, there exist pockets of filler rather than a homogeneous composition; this segregation causes the material to be relatively weak. One possible solution to this problem would be to reverse the system. In such a system, the major component would be the fibrous material and the liquid would be added only in an amount sufficient to saturate the fibers. The fibers would support themselves, thereby keeping segregation to a minimum provided the liquid were suitably contained. Such saturated compositions are suitable for many purposes, but have the disadvantage of being difficult to transport by pumping. In addition, it is economically more attractive to use a liquid, especially water, as the major ingredient particularly in the Arctic where it is available in abundance and the fibrous materials may have to be transported from another area. There are still other differences between the characteristics of the saturated filler and those of the composition comprising water as the major ingredient that make it desirable to use the latter composition.

The desired homogeneous composition comprising water and from 1 to 100 wt. precent based upon the weight of water of a fibrous filler cannot be readily obtained with some fillers because of the aforementioned problem of segregation. Even if the mixture is frozen quickly in an attempt to avoid substantial segregation, another problem in some instance militates against the use of from 30 wt. percent to 100 percent of fibrous filler. The use of some fibrous fillers, e.g. shredded asbestos, promotes the formation of air bubbles in the pores and on the surfaces of the filler; the air bubbles substantially weaken the resulting frozen composition. Heretofore, the air bubbles have been removed by violent agitation and in some instances by boiling. These means of removing the bubbles are cumbersome and expensive. Moreover, they are not effective above concentrations of about 30 wt. percent filler becuase of the high viscosity of the composition. A prohibitive amount of energy is required to drive the air bubbles out of the high viscosity composition.

It is therefore an object of this invention to provide a method of incorporating relatively large amounts of fibrous filler into a frozen liquid composition.

It is a further object of this invention to provide a method of obtaining substantially homogeneous, frozen compositions comprising water and a fibrous filler.

It is still a further object of this invention to provide a method of obtaining a substantially homogeneous, bubble free frozen composition comprising a liquid and relatively large amounts of a fibrous filler.

Other objects of this invention will become apparent as one reads the following disclosure.

Segregation can be significantly reduced by incorporating a thickening agent into the liquid in a small amount sufficient to increase the viscosity of the liquid. The thickening agent impedes the rate of sinking or floating, as the case may be, of the fibrous filler in the liquid. As a result of the early work, it would seem that the use of a thickening agent would be contraindicated, for it appeared that high viscosities made it more difficult to remove air bubbles; this problem is obviated as discussed hereinafter. Experimentation has indicated that the thickening agent may do more than increase the viscosity of the liquid, or it may be that the increased viscosity aids in the formation of bonds; for tests comparing compositions comprising water, filler, and thickening agents resulted in stronger compositions than the results of tests of compositions consisting of water and filler. This was true even though the latter composition was homogeneous; homogeneity was obtained in the latter composition by quickly freezing a composition comprising water and filler in a laboratory.

Many liquids are suitable for the process described herein provided that the liquid can be frozen with refrigeration means that are available at the place of use. Water is preferred because of its low cost, availability, and relatively high freezing point.

The fillers that are employed in this invention are preferably fibrous fillers such as spun glass, plastic fibers, rock wool, shredded hemp, sawdust (wood fiber), fiberglass, asbestos, paper, grass, hay, and the like. In short, suitable fillers can be made from practically any fibrous material including wastes, scraps, and other inexpensive substances. Fillers should be fibrous. The use of dense or compact fillers in the form of beads, chunks, and fragments does not produce the desired effect. The ratio of fiber length to the diameter of the fiber should be at least 5:1 and preferably greater than 15:1. The strength of the resulting frozen composition is directly proportional to the length of the fibers. However, the fibers must not be too long or pumping of the admixture will be difficult or perhaps even impossible. For most applications the fibers should have an average length of from about ⅛ inch to 6 inches.

The thickening agents of this invention should be soluble in the cold liquid that is used as the major ingredient, and should not be adsorbed by the solid filler to the extent that the thickeners become ineffective. If water is employed, the thickening agent may be a synthetic water-soluble gum such as those materials having a polymeric backbone of cellulose. The thickeners sold under the trade name of Methocel have been found to be particularly effective. Other suitable thickening agents used alone or in combinations include synthetic polymers containing polyacrylamide, isomorphous silicates, polyethylene glycols, and the like. The thickening agents should be added in an amount sufficient to significantly impede the sinking

or floating, as the case may be, of the filler in the liquid. The amount required will depend upon a variety of factors including the type of filler employed, the type of thickener or mixture of thickeners selected, and the temperature of the liquid at time of admixing. However, the thickener should usually be employed in the range of from 0.05 to 5.0 wt. percent based upon the weight of the liquid.

In preparing the composition for freezing, the thickening agent should first be added to the liquid medium and the filler material thereafter incorporated. The use of the thickener significantly reduces, and in some instances completely eliminates, the problem of filler segregation. It permits the obtaining of essentially homogeneous compositions even in those instances where there is a substantial delay between the time of mixing and the time of freezing. The thickener is useful over a broad range of filler concentrations. When certain fillers are used, a substantially homogeneous, bubble-free, frozen composition can be obtained by the use of the thickener. However, certain fillers, for example, asbestos, when used in amounts in excess of 30 wt. percent based upon the amount of liquid employed, promote the formation of air bubbles which adhere to the solid surfaces and which heretofore could not be removed from the system without expending a prohibitive amount of energy.

The air bubble problem is greatly reduced and in many cases eliminated in accordance with this invention by utilizing a wetting agent. Known wetting agents are suitable. For example, if water is the liquid, suitable wetting agents include anionic agents such as sodium benzene sulfonate, short chain C_6–C_{10} alkyl aryl sulfonates, short chain dialkyl sulfosuccinates, and short chain alkyl sulfates; nonionic compounds such as C_6–C_{10} fatty acid polyglycol esters, and alkyl aryl polyglycol esters and their derivatives can also be employed. These wetting agents are preferred, but are not the only agents that can be employed. Other agents can be used without departing from the scope of this invention.

The following examples illustrate specific methods of obtaining the objects of this invention.

Example 1

A thickening agent, sodium carboxymethyl cellulose, is dissolved into water in the amount of 1.0% based upon the weight of water. To the solution is added 15 wt. percent (based upon the weight of water) of short plastic fibers. The mixture is thoroughly agitated to obtain a homogeneous admixture of filler in water. The admixture is then frozen and will be homogeneous despite a time delay that is ordinarily encountered when such material is used to construct facilities.

Example 2

0.5 wt. percent of a thickener, sodium carboxymethyl cellulose, is dissolved in water together with 0.5 wt. percent of a wetting agent, sodium dioctyl sulfosuccinate, and 50 wt. percent (based upon the weight of water) of shredded asbestos is thoroughly admixed with the water solution. The admixture is then frozen and there results a homogeneous, bubble-free admixture despite the fact that asbestos ordinarily promotes the formation of air bubbles in water.

Example 3

0.2 wt. percent of a wetting agent, sodium dioctyl sulfosuccinate, is dissolved in water. Thereafter, 40 wt. percent of shredded rock wool, a fibrous filler which ordinarily remains suspended in water without the aid of a thickener and which ordinarily promotes the formation of air bubbles, is thoroughly admixed into the water solution. After freezing, the resulting composition is homogeneous and bubble free.

The invention has been described herein with a certain degree of particularity. Various deviations can be made to the concepts described herein without departing from the scope of the invention.

What is claimed is:

1. A method of obtaining a strong, substantially homogeneous and bubble-free frozen admixture of liquid and a relatively large amount of fibrous filler which ordinarily does not remain suspended in said liquid once dispersed therein and which ordinarily promotes the formation of air bubbles in the admixture comprising: dissolving a thickening agent into said liquid in an amount sufficient to increase the viscosity of said liquid, dissolving a wetting agent into said liqud in an amount sufficient to ensure the wetting of said fibrous filler by said liquid, admixing a fibrous filler into said liquid to obtain a substantially homogeneous admixture, and freezing said admixture.

2. A method of obtaining a strong, substantially homogeneous and bubble-free, frozen admixture of water and a relatively large amount of fibrous filler which ordinarily does not remain suspended in water once dispersed and which ordinarily promotes the formation of air bubbles in the admixture comprising: dissolving a thickening agent into water in an amount sufficient to increase the viscosity of said water, dissolving a wetting agent into the water in an amount sufficient to decrease the surface tension of the water, admixing said fibrous filler in an amount of from 30 wt. percent to 100 wt. percent based upon the weight of water into the water containing the thickening agent and wetting agent to obtain a substantially homogeneous admixure, and freezing said admixture.

3. A method according to claim 2 wherein said admixture is formed into a structural element prior to the freezing of said admixture.

4. A method according to claim 2 wherein said wetting agent is sodium dioctyl sulfosuccinate.

5. A method of obtaining a strong, substantially homogeneous, frozen liquid composition comprising: dissolving a thickening agent into water in an amount in the range of from 0.05 to 5.0 wt. percent based upon the weight of the water sufficient to increase the viscosity of the water, admixing a fibrous filler into said liquid to obtain a substantially homogeneous admixture forming said substantially homogeneous admixture into a structural element, and freezing said admixture.

6. A method of obtaining a strong, substantially homogeneous, frozen liquid composition comprising: dissolving a sodium carboxymethyl cellulose thickening agent into water in an amount sufficient to increase the viscosity of the water, admixing a fibrous filler into said liquid to obtain a substantially homogeneous admixture, forming said substantially homogeneous admixture into a structural element, and freezing said admixture.

References Cited by the Examiner

UNITED STATES PATENTS

1,415,325	2/1919	Ellis	62—1 X
2,291,680	8/1942	Billner	62—1 X
2,793,963	5/1957	Tym	62—66 X
2,800,456	7/1957	Shepherd	62—1 X
3,205,665	9/1965	Van Horn	61—.5

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