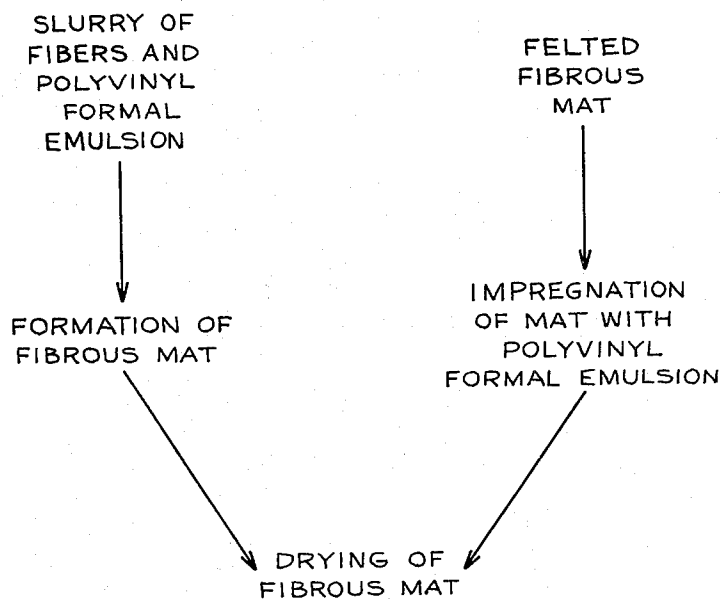


June 30, 1964

M. G. DE FRIES ETAL
PROCESS FOR MAKING A FIBROUS CELLULOSE AND/OR
NITROCELLULOSE PRODUCT
Filed Jan. 22, 1962

3,139,355



INVENTORS.

MYRON G. DE FRIES
JOHN N. GODFREY

BY

Martha L. Ross

AGENT

1

3,139,355

PROCESS FOR MAKING A FIBROUS CELLULOSE AND/OR NITROCELLULOSE PRODUCT

Myron G. De Fries, Bethesda, Md., and John N. Godfrey, Washington, D.C., assignors to Atlantic Research Corporation, Fairfax County, Va., a corporation of Virginia
Filed Jan. 22, 1962, Ser. No. 167,976
17 Claims. (Cl. 117—155)

This invention relates to a new and improved process for making fibrous, felted material of high structural strength and combustibility. More specifically, it relates to the manufacture of combustible casing material for propellant and explosive powders and grains.

Consumable cartridge casings made of felted cellulose fibers have long been in use. Such paper casings are, however, relatively slow-burning and contribute little, if at all, to the production of propulsive combustion gases. It has recently been proposed that the cellulose fibers be admixed with fibers of nitrocellulose to provide a casing material which burns more rapidly and completely and produces an additional increment of thrust. The addition of the fibers of nitrocellulose, however, introduces processing problems because of its sensitivity to elevated temperatures and its relative incompatibility with many of the bonding adhesives conventionally employed to increase the structural strength and moisture resistance of paper products. The nitrocellulose tends to degrade or decompose and, in so doing, produces corrosive products which attack the cellulose fibers.

The object of this invention is to provide a safe and simple process for making felted sheets or other structures of superior strength and moisture resistance from cellulose, nitrocellulose fibers or a mixture of cellulose and nitrocellulose fibers bonded and moisture-proofed by means of a polyvinyl formal resin.

Broadly speaking, the invention comprises impregnating a pre-formed web or mat of cellulose fibers, nitrocellulose fibers or intermingled cellulose and nitrocellulose fibers with an aqueous oil-in-water type emulsion of polyvinyl formal dissolved in a volatile solvent which is substantially immiscible with water and then drying the impregnated web to remove the water and solvent; or, alternatively slurrying the fibers directly into said polyvinyl formal emulsion and then forming the fibrous web and drying.

Polyvinyl formal is particularly effective because of the high strength and moisture-proofness that it imparts to the fibrous web and its high degree of compatibility with nitrocellulose. The formal, which is preferably free from, or contains at most a relatively low percentage of combined acetate, does not adversely affect the stability of nitrocellulose even during long periods of storage and has the additional advantage of maintaining the structural strength of the casing at high temperatures. In general, the polyvinyl formal, which is conventionally produced by reaction of formaldehyde with polyvinyl alcohol, which in turn is conventionally prepared by hydrolysis of polyvinyl acetate, preferably contains at most about 15% by weight of combined acetate expressed as percent polyvinyl acetate.

In conventional applications, polyvinyl formal has hitherto been used in the form of solutions in volatile organic solvents. Such solutions can be employed to impregnate and bond the fibers, but this expedient presents severe processing difficulties. The mixture of fibers which in conventional practice is slurried in water must be first felted into a mat. The mat must then be thoroughly dried before impregnation with the organic solvent solution. The thorough drying of the felted fibers including nitrocellulose is very hazardous because of the high heat

2

sensitivity of the nitrocellulose at this step of the process. Nitrocellulose in fibrous form ordinarily does not contain a stabilizer, such as diphenyl amine, which normally must be incorporated by way of solution in an organic solvent. At this point also, it does not have the desensitizing protection of the bonding resin. Impregnation of the mat and drainage of the saturated web are excessively slow because of the high viscosity of the resin solutions containing adequate concentrations of the polyvinyl formal. Drying of the impregnated web by removal of the volatile solvent is excessively slow because of the decrease in permeability as volatilization proceeds. The polymer solutions also tend to build up tacky deposits in the equipment which are difficult, time-consuming, and costly to remove.

Our process utilizing aqueous emulsions is free of the problems aforescribed. The felted fibers need not be dried before impregnation with the emulsion since both are aqueous systems. To minimize dilution of the impregnating emulsion, excessive amounts of water in the web can be easily drained by applying vacuum or compression. In some cases, the fibers can be slurried directly into the emulsion and then felted, thus eliminating still another step in the process. Since the emulsions have considerably lower viscosity for a given concentration of resin solids than do the organic solvent solutions, impregnation can be accomplished with greater ease and rapidity. Drying of the impregnated mat is also greatly facilitated by the non-solvent property of the water and the greatly reduced amount of volatile organic solvent which must be removed. The latter feature also reduces the hazards inherent in volatilizing large amounts of an organic solvent.

Although the aqueous formal resin emulsions are particularly advantageous for use as impregnants and bonding agents for felted mats containing nitrocellulose fibers, they can also be used very effectively with all cellulose fibers to impart high strength and moisture resistance with a minimum of processing problems.

The cellulose fibers can be any conventionally employed in paper making such as sulfate, sulfite, rag, and groundwood, bleached or unbleached. They can be used in the form of the slurry obtained from the beater, or in the form of dried fibers, which are then reslurried. The nitrocellulose fibers, similarly, can be employed in any commercially available form. The felted web can be made entirely of nitrocellulose fibers. Preferably, it comprises a mixture of nitrocellulose and cellulose fibers. The ratio of nitrocellulose fibers to cellulose fibers will generally be determined by the particular application, and can vary from as little as 5% by weight of total fiber to as much as 99% nitrocellulose fiber content. In general, optimum performance in terms of physical and ballistic properties is obtained with ratios of nitrocellulose/cellulose/formal in the following ranges: 40–70%/5–50%/10–25%.

We have found that an improved product is obtained by use of an emulsion containing a dispersing agent which is volatilized, decomposed into insoluble and/or volatile products, or otherwise insolubilized during the drying process after impregnation of the mat.

We have found particularly suitable for our purpose an oil-in-water type emulsion in which the dispersing agent is a soap formed from a fatty acid and a volatile water-soluble amine. The acid can be any saturated or unsaturated higher fatty acid containing at least 6 carbon atoms and generally up to about 20 carbon atoms, such as caprylic, capric, lauric, palmitic, stearic, oleic, and linoleic acids. The salt or soap-forming amine is preferably a water-soluble, aliphatic primary or secondary amine which can have one or a plurality of amino groups

and a maximum boiling point at 760 mm. Hg of about 140° C. Examples of such amines include alkyl amines, e.g. butyl amine, ethylene diamine, and propylene diamine; aliphatic cyclic amines, e.g. piperidine, morpholine, and methyl morpholine; and the like.

The fatty acid-amine salt can be introduced *per se* into the mixture of emulsion components. Preferably, it is formed *in situ* in the manner which will be described. The latter method ensures the formation of a stable oil-in-water phase dispersion. The concentration of the fatty acid-amine salt dispersing agent may range from about 0.25 to 10% with the preferred range being about 1 to 4 percent.

The emulsions which produce superior results for our purpose are prepared as follows:

The polyvinyl formal is dissolved in a substantially water-immiscible volatile, organic solvent. By substantial water-immiscibility is meant a solvent having a maximum water solubility of about 15% by weight at 20° C., preferably a maximum solubility of about 10%. The solvent desirably has a maximum boiling point of about 115° C., preferably less than 100° C. It will be understood that a co-solvent mixture having, in combination, these physical properties can also be used. Volatile organic solvents for the formal resins are well-known in the art and can readily be found in available literature. Ethylene dichloride is particularly suitable for use with the low acetate content formal. The formal resin is dissolved in an amount determined largely by the desired resin solids content required by the particular application. In general, this will range from about 5 to 50% by weight of the organic solvent solution.

While the formal resin generally does not require the addition of a plasticizer, such modifiers can be incorporated if desired. The plasticizers, which are generally high boiling organic liquids, can be preblended with the resin or can be introduced by way of admixture with the volatile organic solvent. Addition of organic liquid plasticizer to the volatile organic solvent has the advantage of reducing the amount of volatile solvent required to produce adequate solution fluidity.

A large variety of suitable plasticizers are known in the art and include, for example, phthalic acid esters, e.g. diethyl, dicyclohexyl and diphenyl phthalate; adipic acid esters, e.g. dibutoxyethyl adipate; organic phosphate esters, e.g. tributyl, tricresyl and triphenyl phosphate; glycolates, e.g. butyl phthalyl butyl glycolate. The amount of plasticizer is not critical, but is largely determined by the requirements of a particular application and the properties of the particular plasticizer. In general, the maximum amount is about 40% by weight of the resin, preferably a maximum of about 20%.

The salt-forming, water-soluble amine as *aforedescribed*, preferably in stoichiometric to excess amounts relative to the fatty acid, is separately dissolved in water. This solution is then added slowly and with continuous agitation to the formal solution. After addition of the aqueous amine solution is completed, more water can be added to bring the emulsion to the final desired solids concentration. The oil-in-water type emulsion formulated in this manner is stable at ordinary to reduced temperatures at ambient to elevated pressures. At elevated temperatures, such as those employed to dry the felted mats after impregnation with the emulsion, or under vacuum, the fatty acid-amine salt decomposes into the water-insoluble fatty acid and volatile amine, leaving an insoluble fatty acid residue which improves moisture resistance.

Example 1

Mix well 50 grams of polyvinyl formal resin (Formvar 7/95S containing about 9.5–13% acetate expressed as polyvinyl acetate) and 100 grams of ethylene chloride. Heat and agitate to achieve uniform solution and cool to room temperature. Add 6 grams of oleic acid with agitation. Add 2 grams of morpholine dissolved in 40 grams of water slowly with agitation to the resin solution. Add

with agitation 202 g. of water to give a final emulsion having the composition: 12.5% Formvar 7/95S, 60.5% water, 25.0% ethylene chloride and 2.0% dispersing agent (the morpholine salt of oleic acid).

The emulsion can be applied to the felted fibers in any suitable manner, as by dipping, or by drawing it through the web by suction. The amount of formal resin added on is determined largely by the requirements of the final use and can range from 2 to 50% by weight of the fibers, preferably about 10 to 25% by weight. The actual amount of resin retained in the dried felt is a function of the solids content of the impregnating medium, subsequent extraction of excess emulsion, as by pressing, and on the porosity of the felt prior to impregnation. These factors should, of course, be determined by routine test and the solids content of the impregnating emulsion adjusted accordingly.

Drying of the impregnated fibrous mat is accomplished under vacuum or by heating at moderately elevated temperatures which will be determined to a considerable extent by the presence and concentration of nitrocellulose fibers. Although sensitivity of the nitrocellulose is very much reduced by the formal resin and the stabilizer introduced in the oil phase of the emulsion, excessively high temperatures approaching the auto-ignition temperature of the ballistic composition must, of course, be avoided. Webs comprising nitrocellulose generally should not be dried at temperatures higher than about 185° F. In the absence of nitrocellulose, higher drying temperatures can be employed. Alternatively, drying can be accomplished by applying a vacuum with or without heating.

Example 2

6.6 g. dry kraft fiber were slurried in 1750 cc. water and beaten in an Osterizer for 1 minute. 20 g. water-wet nitrocellulose fibers (smokeless, 12.6% N, 5 sec., approximately 25% water) were added to 1750 cc. water and beaten in the Osterizer for 1 minute. The two slurries were then mixed.

The fiber mats were prepared by filtering 1 liter of the above slurry through a Büchner funnel under vacuum using 50 mesh wire screen to retain the fibers. Excess water was removed by pulling air through the mat with continued application of the vacuum after all of the slurry liquid has passed through.

The fiber mat in the Büchner funnel was covered with an emulsion prepared as described in Example 1, but comprising 20.29% polyvinyl formal, 44.64% ethylene chloride, 32.47% water, and 2.6% fatty acid-amine soap emulsifier (1.95% oleic acid and 0.65% morpholine). A slight vacuum was applied until the mat was impregnated and the fluid began to pass through. The vacuum was then increased to remove excess emulsion. The latex drained through instantaneously. The impregnated mat was removed from the funnel, pressed for 1 minute at 200 p.s.i., using a Carver press, and then oven dried for 1 hour at 165° F.

Mats prepared in this manner were uniformly impregnated, tough, hard, smooth-surfaced, and moisture-proof. Tests on a Tinius-Olsen testing machine showed excellent strength and good elongation:

Maximum tensile stress	-----p.s.i.---	2621
Elongation at maximum stress	-----percent---	8.1

The mats ignited and burned very satisfactorily.

As *aforementioned*, the mats can also be prepared by slurrying the fibers directly into the emulsion and then felting the already impregnated fibers. Because of the increased viscosity imparted to the emulsion by the added fibers, this method is best implemented with an emulsion in which the oil phase (solution of formal resin in volatile organic solvent) has a high resin concentration.

Although this invention has been described with reference to illustrative embodiments thereof, it will be apparent to those skilled in the art that the principles of this

invention may be embodied in other forms but within the scope of the appended claims.

We claim:

1. In a process for making a felted, fibrous product comprising fibers selected from the group consisting of cellulose, nitrocellulose, and mixtures thereof, the improvement comprising impregnating said fibers with an aqueous oil-in-water type emulsion comprising a solution of polyvinyl formal in a volatile organic solvent having a maximum solubility in water of about 15% by weight at 20° C., dispersed in water, said polyvinyl formal comprising about 2% to 50% by weight of said fibers, and then drying said impregnated mixture of fibers.

2. In a process for making a felted fibrous product comprising a mixture of cellulose and nitrocellulose fibers, the improvement comprising impregnating said mixture of fibers with an aqueous oil-in-water type emulsion comprising a solution of polyvinyl formal in a volatile organic solvent having a maximum solubility in water of about 15% by weight at 20° C., dispersed in water, said polyvinyl formal comprising about 2% to 50% by weight of said fibers, and then drying said impregnated mixture of fibers.

3. The process of claim 2 in which the polyvinyl formal has a maximum acetate content expressed as polyvinyl acetate of about 15% by weight.

4. The process of claim 2 in which said impregnated mixture of fibers is dried at elevated temperatures and the emulsion contains about 0.25% to 10% by weight of a water-soluble dispersing agent decomposable into a water-insoluble state at said elevated temperatures.

5. The process of claim 3 in which said impregnated mixture of fibers is dried at elevated temperatures and the emulsion contains about 0.25% to 10% by weight of a water-soluble dispersing agent decomposable into a water-insoluble state at said elevated temperatures.

6. The process of claim 4 in which the water-soluble dispersing agent is the salt formed from a fatty acid containing at least 6 carbon atoms and a volatile, water-soluble, aliphatic amine.

7. The process of claim 5 in which the water-soluble dispersing agent is the salt formed from a fatty acid containing at least 6 carbon atoms and a volatile, water-soluble, aliphatic amine.

8. The process of claim 6 in which the fatty acid-amine salt is formed in situ in the emulsion by dissolving the fatty acid in the polyvinyl formal solution in organic solvent and by dissolving the amine in water and then ad-

mixing said organic solvent solution and said solution of amine in water.

9. The process of claim 7 in which the fatty acid-amine salt is formed in situ in the emulsion by dissolving the fatty acid in the polyvinyl formal solution in organic solvent and by dissolving the amine in water and then admixing said organic solvent solution and said solution of amine in water.

10. The process of claim 8 in which the fatty acid is oleic acid and the amine is morpholine.

11. The process of claim 9 in which the fatty acid is oleic acid and the amine is morpholine.

12. The process of claim 1 in which the emulsion contains about 0.25 to 10% by weight of a water-soluble dispersing agent decomposable into a water-insoluble state during drying of said impregnated mixture of fibers.

13. The process of claim 2 in which the emulsion contains about 0.25 to 10% by weight of a water-soluble dispersing agent decomposable into a water-insoluble state during drying of said impregnated mixture of fibers.

14. The process of claim 13 in which the polyvinyl formal has a maximum acetate content expressed as polyvinyl acetate of about 15% by weight.

15. The process of claim 14 in which the water-soluble dispersing agent is the salt formed from a fatty acid containing at least 6 carbon atoms and a volatile, water-soluble, aliphatic amine.

16. The process of claim 15 in which the fatty acid-amine salt is formed in situ in the emulsion by dissolving the fatty acid in the polyvinyl formal solution in organic solvent and by dissolving the amine in water and then admixing said organic solvent solution and said solution of amine in water.

17. The process of claim 16 in which the fatty acid is oleic acid and the amine is morpholine.

References Cited in the file of this patent

UNITED STATES PATENTS

2,011,914	Schwartz	Aug. 20, 1935
2,482,237	Berglund	Sept. 20, 1949
2,484,023	Fenimore et al.	Oct. 11, 1949
2,666,038	Eisen	Jan. 12, 1954
2,876,136	Ford	Mar. 3, 1959
2,991,168	Nadel	July 4, 1961

FOREIGN PATENTS

542,854	Great Britain	Jan. 29, 1942
---------	---------------	---------------