Patented Sept. 27, 1938

2,131,040

# UNITED STATES PATENT OFFICE

2,131,040

## FIBER TREATMENT AND PRODUCT

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No Drawing. Application May 11, 1937, Serial No. 142,070

10 Claims. (Cl. 21—26)

The present invention relates to a treatment of bast and structural fibers, whereby the fibers are rendered more resistant to attack by deleterious organisms, such, for example, as algae, bacteria and/or fungi, and to the resulting product.

The cells of both bast and structural fibers consist essentially of cellulose in association with various alteration products, such as lignin, cemented together by a water-insoluble pectinous material and compacted to form an individual fiber. Examples of bast fibers, derived from the inner fibrous bark of dicotoledenous plants, are flax, ramie, jute, etc. Examples of structural fibers, derived from the stalks, leaf stems and leaves of moncotoledenous plants, are sisal, manila, sanseveria, etc.

It is an object of the present invention to provide an improved method of treating bast and structural fibers, whereby they are rendered more resistant to the damaging attacks of organisms, such for example as algae, bacteria and/or fungi. The invention also comprehends an improved fibrous product

By the process of this invention a toxic compound of copper is deposited within the cementing substance of the fiber without significant impairment of the tensile strength of the fiber.

My treatment may advantageously be applied to bast and structural fibers or fabrics comprising such fibers, such, for example, as cordage, sacking or other fabrics (the word "fabric" being used in its broadest sense to designate any fabricated article or material) in any case where the fibers or fabrics are exposed to the attacks of algae, bacteria and/or fungi.

The attacks of algae, bacteria and filamentous fungi upon bast and structural fibers are the cause of great economic loss. The resulting deterioration of the fibers has been ascribed to the action of the organisms upon the water-soluble constituents of the fibers, giving rise to various acid products which in turn act on the insoluble parts, changing them further into bacterial food.

The value of a toxic, in the case of vegetable fibers, depends not only upon its ability to control the attacks of organisms, but also upon its harmlessness to the tissues, both at the time of impregnation and during subsequent exposure.

Copper compounds are toxic to many forms of life, but their use in the class of fibers under consideration has hitherto been unsuccessful, so far as I am aware. The failure to effect a satisfactory impregnation without loss of tensile strength may be attributed to the fact that cellulose is negatively charged, and the cementing pectinous substance is readily hydrolyzed by acids. Permanent protection requires the fixation of the toxic in an insoluble form upon the cellulose. Penetration of the pectinous substance by a soluble copper salt must therefore first occur and be followed by the penetration of a substance which will precipitate an insoluble copper compound within the fiber.

Insoluble copper sulfide is formed when a solution of a copper salt is treated with a solution containing sulfide ions. Since, however, copper sulfide is negatively charged, it is not adsorbed by the negatively charged cellulose, unless the latter has first been treated with a mordant, i. e., a substance which will impose upon the cellulose a positively charged substance. While preliminary treatment with mordants can be applied to pure cellulosic fibers such as cotton, in the case of bast and of structural fibers, it has a deleterious hydrolytic effect upon the cementing substance, with resulting solution and disintegration, the fiber being thus broken up into its elements with a corresponding loss in tensile strength.

I have found that these and other difficulties may be avoided and that bast and structural fibers may be effectively and satisfactorily treated to increase their resistance to deleterious organisms such as algae, bacteria and/or fungi if the fibers be first treated with a weak acid associated with a copper salt corresponding to the acid used, and subsequently treated with a soluble sulfide.

By this treatment copper sulfide is formed within the confines of the enveloping pectinous cement. This obviates the difficulty of application arising from the insolubility of copper sulfide if this compound be formed before impregnation. In my process, penetration of the fiber by the copper solution first occurs, followed by penetration by the sulfide. Further, in my process the imposition of a mordant, which imposes a positively charged substance on the cellulose and which is advantageous in impregnation of the fiber, is accomplished without deleterious alteration of the chemical composition of the cellulose constituent while maintaining the insolubility of the cementing substance.

No apparent loss in tensile strength results from treatment of bast and structural fibers in accordance with my invention. Precipitation of the copper compound within the fiber seems to occur, with probable adsorption by the cellulose. Prolonged leaching, both in fresh and in sea water, of fibers treated in accordance with my invention shows no loss of the color imparted by the copper sulfide.

Acids suitable for use in my process should ionize less than 10% in normal solution. Acetic acid is preferred, but other weak acids which ionize less than 10% in normal solution may be used. For example, malic or tartaric acid may be used. These latter acids, however, will crystallize in the fibers and thereby weaken the structure unless the crystals are removed. Therefore, if acids which crystallize in the fiber are used,

the crystals should be washed out after the treatment. To avoid this washing operation, it is preferred to use acids such as acetic acid which do not crystallize in the fibers.

As previously indicated, the copper salt to be selected is that corresponding to the acid used,—i. e., with an acetic acid solution copper acetate will be used. In such a solution there is present the "common ion effect" by which the degree of ionization and momentary acidity or alkalinity of a slightly active acid or base are decreased by the addition of their salts. Acetic acid, for example, is but slightly dissociated (reaction *a*):

$$HC_2H_3O_2 \underset{b}{\overset{a}{\rightleftharpoons}} H + C_2H_3O_2$$

By adding the moderately ionized copper acetate to the acetic acid solution, I provide an extra supply of acetate ions, thus, by the law of mass action, favoring reaction *b* in the above equilibrium. Thus the small momentary acidity of the acetic acid is still further decreased and its reserve acidity is increased, while the total acidity remains practically unchanged.

Hydrogen-ion measurements show a pH value of N/10 acetic acid of 2.9; of normal copper acetate in N/20 solution of 6.6. A mixture containing the same amounts of the two shows a pH of 4.8. Tests on various fibers finely shredded gave the following:

| | pH |
|---|---|
| Jute | 4.2 |
| Sisal | 4.6 |
| Ramie | 4.6 |
| Manila | 4.8 |
| American flax | 4.8 |
| American hemp | 4.8 |

If it be assumed that the above values represent the hydrogen-ion concentration at which the pectinous cement of the various fibers is least soluble, and consequently the tensile strength best maintained for the purpose of the plant, an explanation is afforded for the observations previously noted when this class of fibers is treated with the copper acetate-acetic acid mixture, and subsequently with the sulfide solution. Copper and hydrogen ions pass through the essentially unaltered cementing membrane and come into contact with the cellulose. From the viewpoint of physical chemistry, the negatively charged cellulose becomes mordanted by the hydrogen ions and adsorbs the copper sulfide precipitated by the subsequently applied sulfide solution.

My process provides a valuable method of precipitating a toxic compound of copper within the cementing substance of the fiber and causing the toxic to become fixed upon the cellulose without impairment of the tensile strength.

As previously indicated, my process comprises treatment of the fibers with a solution of a weakly ionized acid and its corresponding copper salt, followed by the application of a soluble sulfide (such, for example, as hydrogen sulfide) or a solution containing sulfide ions, whereby copper sulfide is deposited upon and within the structural elements of the fiber.

As a specific example of one suitable procedure, the following may be given, it being understood that this is by way of example only and is not to be construed in a limiting sense: The fibers are immersed in a N/10 solution of acetic acid and a N/20 solution of normal copper acetate for several hours at a temperature preferably between 60 and 80 degrees Fahrenheit, with sufficient agitation of the liquid to dislodge adherent particles of air. After this period the fibers are rinsed in water to remove superfluous impregnating fluid from their surfaces, and immersed in a N/10 solution of mono-sodium sulfide for several hours. The treatment is completed by a final rinsing and drying.

I claim:

1. A process for the treatment of bast or structural fibers which comprises treating the fibers with an acid which in normal solution ionizes less than 10% and with a copper salt corresponding to the acid used, then treating the fiber with a soluble sulfide.

2. The method of treating bast or structural fibers which comprises impregnating such fiber with a solution of an organic acid which in normal solution ionizes less than 10%, said solution also containing a salt of copper corresponding to the anion of the acid, and subsequently impregnating the fiber with a solution containing sulfide ions.

3. The method of treating bast or structural fibers which comprises treating such fiber with a solution comprising acetic acid and copper acetate, then treating the fiber with a solution containing sulfide ions, whereby the resistance of the fiber to attack by deleterious organisms is increased.

4. The method of treating bast or structural fiber to render the same more resistant to attack by deleterious organisms, which comprises treating the fiber with a solution comprising acetic acid and copper acetate, then treating the fiber with a solution of mono-sodium sulfide.

5. The treatment of bast or structural fiber to increase the resistance of the fiber to attack by deleterious organisms, which comprises immersing the fiber in a solution containing acetic acid and copper acetate, rinsing the fiber, impregnating the fiber with a solution of a soluble sulfide, then rinsing and drying the fiber.

6. The treatment of bast or structural fibers which comprises immersing the fibers in an approximately N/10 solution of acetic acid and an approximately N/20 solution of copper acetate at a temperature between approximately 60 and 80° F., agitating the liquid, and subsequently immersing the fibers in an approximately N/10 solution of mono-sodium sulfide.

7. As a new article of manufacture, a fabric comprising fibers which consist essentially of cellulose associated with water-insoluble pectinous material, said fiber being of substantially unimpaired tensile strength and containing copper sulfide.

8. As a new article of manufacture, bast or structural fiber of substantially normal tensile strength, said fiber containing copper sulfide within the cementing substance of the fiber.

9. A process for the treatment of bast or structural fiber which comprises treating the fiber with an acid which in normal solution ionizes less than 10% and with a copper salt corresponding to the acid used, then treating the fiber with hydrogen sulfide.

10. The method of treating bast or structural fiber which comprises treating the fiber with acetic acid and copper acetate, then treating the fiber with hydrogen sulfide.

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