UNITED STATES PATENT OFFICE.

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PYROXYLIN COMPOUND.

SPECIFICATION forming part of Letters Patent No. 612,531, dated October 18, 1898.

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To all whom it may concern:

Be it known that I, JOHN H. STEVENS, of the city of Newark, county of Essex, and State of New Jersey, have invented certain new and useful Improvements in Pyroxylin Compositions of Matter, of which the following is a specification.

Pyroxylin is a substance well known as the product obtained by treating cellulose fiber with mixtures of nitric and sulfuric acids. The cellulose is generally employed in the form of cotton or paper. The pyroxylin products so obtained present great variety in the amount of nitro elements which the cellulose has absorbed during the acid treatment, and the amount of these nitro elements in the pyroxylin, together with the conditions of treatment, determines the solubility, inflammability, or explosiveness of the pyroxylin.

The most highly nitrated pyroxylins are explosive and of little or no solubility in the usual solvents, such as ether alcohol, camphor spirits, and wood-spirit. The lower-nitration products, while inflammable, are relatively non-explosive, and they are also soluble in the various pyroxylin solvents, such as those mentioned.

The highly-explosive pyroxylin is known as "guncotton" and has been used in the pure or fibrous state in blasting and as an explosive in warfare. The soluble varieties have been dissolved in appropriate solvents and used as varnishes, lacquers, or waterproofing solutions, or in stiffer masses, and in connection with dyes or pigments for the purpose of making compounds in imitation of various natural and other substances, such as ivory, tortoise-shell, glass, amber, jet, starched linen, &c.

The improvements in smokeless powder have led to the use of practically all the grades of pyroxylin, the intensity or rapidity of combustion being controlled by a suitable admixture of the highly-inflammable with the explosive varieties. The guncotton used in making explosive gelatin lies midway between the high and the low nitration products, and is a special and definite compound which gelatinizes with nitroglycerin or is soluble in that menstruum. The explosiveness and inflammability of all these pyroxylins are largely modified by the presence of solvents or other substances used as deterrents. When pure and well washed, the different grades of pyroxylin are neutral—that is, they possess no acid reaction. Nevertheless they are subject to an acid decomposition, especially under the influence of time or elevated temperature.

Attempts have been made to purify or treat the pyroxylin in such a way as to minimize their tendency to disorganization; but while the most carefully made or most highly purified pyroxylin has been known to last for years without turning acid numerous fatal accidents have occurred in storing guncotton in a dry state, and pyroxylin compounds made with the aid of solvents have been more or less affected by the acid evolved in the course of time, so that finally inventors turned their attention to the preservation of pyroxylin or its compounds by the introduction of some element which would neutralize the acid or, by its presence, hinder or prevent its decomposition. This required considerable selection and experimenting, because pyroxylin is a peculiar product, and some substances which might be supposed to act as neutralizers or antacids often have the opposite effect when introduced into these compounds—that is, they sometimes even invite decomposition. Therefore, even when a substance is known to possess antacid power it is necessary to mix it with pyroxylin or its solutions and observe the effects before it can be known that its antacid power is of use in connection with pyroxylin. For instance, the art did not know the compatibility of urea and pyroxylin until pyroxylin was dissolved in a solution of the urea, and the solvent power, perfect transparency, and color effects were observed. As a consequence of these facts numerous substances have been tried and rejected, and the art is in possession of but very few successful preserving agents for pyroxylin, and even these, by reason of their peculiar properties or reaction with the pyroxylin, are often more or less objectionable.

The numerous and varied applications of

pyroxylin compounds necessitate special properties, such as color, transparency, action on metals or other substances, and susceptibility to light and heat. Pyroxylin is a sensitive compound, and in applying antacid substances the operator meets many difficulties by reason of this tendency of pyroxylin to change and the necessities of the different applications of his mixtures. Consequently an enlargement of the list of useful antacids for these purposes is necessary and desirable.

The object of the present invention is to furnish the art with a new group of substances to be used with pyroxylin or its various compounds for the purpose of preserving them against deterioration or chemical changes caused by acid decomposition. This new group consists of the lithium salts of the volatile monatomic fatty acids. The principal acids of this group are formic, acetic, propionic, butyric, and valeric acids. The salts resulting from the chemical combination of these acids with lithium are lithium formate, lithium acetate, lithium propionate, lithium butyrate, and lithium valerate. I have used these salts successfully and have determined by experiment their relative value for the purpose. While they all possess more or less antacid power, I prefer to use the salts which are most easily soluble, especially in alcohol or wood-spirit, because these are the solvents most commonly used in the art. While an ordinary mechanical mixture of the preserving agent with the pyroxylin compounds is sufficient to impart stability, the employment of a solution of the salt permits a better distribution, so that every part of the pyroxylin or its compounds is protected by reason of intimate contact with the salt. In making these compounds for the different purposes for which they are used I find that lithium acetate is preferable.

In applying my invention I treat pyroxylin which is to be used or sold in the fibrous form by means of a solution of lithium acetate in water or other menstruum that does not dissolve the pyroxylin. On evaporating the water the pyroxylin is left in a dry condition, but thoroughly impregnated with the lithium acetate, and therefore safer to transport, store, and handle. It is understood, however, that in the absence of solvents or other deterrents the pyroxylin is in a very sensitive condition. The preserving agent does not reduce the inflammability or explosiveness of the pyroxylin. It simply preserves it against dangerous chemical changes, or at least reduces these tendencies to a minimum. In making flowable compounds, such as varnishes or waterproofing solutions, I introduce the lithium acetate dissolved in alcohol or wood-spirit. In making stiffer compounds, such as those which contain so little solvent that they have to be masticated in rolls or other machinery, I introduce the antacid salt, preferably in solution, either in wood-spirit or grain-alcohol, although it can be employed in the form of powder, in which case mastication with the solvent and other ingredients results in a thorough incorporation of the salt. In making acetone solutions, such as smokeless-powder mixtures, I recommend that the lithium acetate or other salt be dissolved in wood-spirit before it is added.

As to proportions, I find that one per cent., by weight, of the salt to the pyroxylin is sufficient for good results. I have discovered in operating with these salts that those which dissolve most readily in the solvent used to form the compounds are the most powerful in their preserving effects. The formate of lithium is not as strong in antacid power as the acetate, is less easily soluble, and gives only a moderate transparency.

I would recommend that the formate of lithium be confined to products like explosives, in which high transparency is not specially desired and which are not to be subjected to severe conditions of treatment in their manufacture—like heat, for instance. Nevertheless it is a fair antacid.

The propionate, butyrate, and valerate of lithium are as powerful in preserving effects as the acetate. The butyrate and valerate have a more or less offensive odor, which is absent in the other salts. I have employed lithium acetate with considerable success in forming pyroxylin sheets of high transparency. It is especially useful in tortoise-shell effects. These lithium salts possess other advantages over some of the antacids heretofore used. For instance, pyroxylin compounds made with urea are sometimes contaminated by a product resulting from the reaction between the urea and the nitro element present. This product is presumably nitrate of urea. At any rate, compounds made with urea when subjected to severe treatment, like heat in contact with metal plates, are liable to a smearing of the surface of the sheets and a staining or smutching of the polishing-plates or metal dies. Urea-pyroxylin compounds are also apt to blister easily under heat. In using these salts of lithium, especially the preferred ones, like lithium acetate, these defects do not occur, and imitation tortoise-shell sheets, for instance, made with lithium acetate as the preserving agent, present a better surface and the polishing-plates last longer than is the case with urea compounds.

For explosives and some of the other pyroxylin compounds the qualities of color and transparency or the action of the by-products in molding, &c., are unimportant and the antacid or preserving effect is all that is desired, although even in opaque compounds the properties of these new antacids are sometimes desirable. For instance, the use of lithium acetate or others of the more soluble salts permits a special improvement in black effects. An imitation of jet made with

lithium acetate possesses a deeper hue than the black compounds containing carbonate of magnesia or other insoluble antacids.

I have found that the salts of this new group are capable of producing effects beyond a mere preservation of pyroxylin and its compounds against decomposition, which effects render them specially useful in forming transparent compounds in imitation of tortoise-shell or amber and in making transparent sheeting.

The art of manufacturing pyroxylin compositions is sufficiently well known, and it is therefore unnecessary for me to state any more in regard to the different mixtures, manipulations, and applications of pyroxylin and its compounds. Obviously I do not confine myself to any particular proportions. Less than one per cent. of the lithium salt to the pyroxylin will give less stability, and more than one per cent. will give increased stability up to the point where the presence of the salt will tend to weaken the compound by imparting too much of its own physical properties to the result. I would not recommend more than two per cent. unless the salts are needed in excess on account of some other peculiar property, and in compounds like "celluloid" I find that one per cent. is a good general proportion, especially as one per cent. gives the palest color effects.

While I am unable to explain why a basic substance already saturated with an acid can act as a preserving agent and prevent the deleterious action of the corrosive nitro compounds in decomposing pyroxylin, my experiments have nevertheless demonstrated this to be a fact. I can only state that it seems to depend on the nature of the acid radical present in the preserving agent. Even when the elements contained in these preserving-salts are united to other substances—for instance, in neutral salts containing dissimilar acid radicals—the resultant compound salt possesses preserving power at least in proportion approximating to the amount of such element present. As an instance of the effect of the nature of the acid radical present in these preserving-salts I can state that I have found by experiment that while acetate of lithium is a good antacid substance in connection with pyroxylin sulfate of lithium has little or no antacid power. Similarly, I find that salts containing two or more bases are good preservers, according to the properties of their constituents. I include in my invention the present group of lithium salts of the volatile monatomic fatty acids as preserving agents for transparent pyroxylin compounds, whether the salts are simple, compound, mixed, or combined chemically with other salts.

By transparent pyroxylin compounds I mean those solids and liquid solutions which permit the transmission of light—for instance, transparent sheets, rods, or articles in imitation of amber, glass, tortoise-shell, and horn, and clear solutions used for varnishes, lacquers, waterproofing-coatings, or the making of sheets or films by the evaporating process.

Having fully instructed the operator in my invention, what I claim, and desire to secure by Letters Patent, is—

1. A pyroxylin composition of matter consisting of pyroxylin associated with a lithium salt of a volatile monatomic fatty acid, substantially as described.

2. A pyroxylin composition of matter consisting of pyroxylin and a solvent of the same associated with a lithium salt of a volatile monatomic fatty acid, substantially as described.

3. A pyroxylin composition of matter containing pyroxylin and acetate of lithium.

4. A transparent pyroxylin composition of matter consisting of pyroxylin associated with a lithium salt of a volatile monatomic fatty acid, substantially as described.

5. A transparent pyroxylin composition of matter consisting of pyroxylin and a solvent of the same associated with a lithium salt of a volatile monatomic fatty acid, substantially as described.

6. A transparent pyroxylin composition of matter containing pyroxylin and acetate of lithium.

JOHN H. STEVENS.

Witnesses:
ABRAHAM MANNERS,
JOHN W. HOWARTH.