UNITED STATES PATENT OFFICE.

JOHN H. STEVENS, OF NEWARK, NEW JERSEY, ASSIGNOR TO THE CELLULOID COMPANY, OF NEW YORK, N. Y.

COMPOUND OF PYROXYLIN.

SPECIFICATION forming part of Letters Patent No. 543,197, dated July 23, 1895.

Application filed May 31, 1895. Serial No. 551,285. (No specimens.)

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 Compounds, of which the following is a specification.

The class of pyroxyline compounds to which my invention relates are known in commerce, mainly, as imitations of natural substances, and are especially valuable by reason of their plasticity under heat when in a dried or seasoned condition. They are commonly formed by combining soluble pyroxyline with camphor by the aid of a liquid solvent or menstruum, and coloring materials or other substances are incorporated with them to produce the appearance or character of the product desired. The most popular methods employed to form these compounds involve the use of a minimum proportion of solvent, which will, by the aid of heat, pressure, and mastication, permit the pyroxyline to be converted into a solid mass of material. Another method is to evaporate down a liquid solution to form thin films or sheets or masses built up by successive applications and dryings of liquid solutions. This method has a limited application, however, due to the waste of solvent and incidental imperfections. In all cases the value of the compound is in the final dried product, whether it be thin films or sheets or thick masses. Two classes of solvents are employed—liquid and solid. The liquid solvents are generally of a volatile nature, and during the curing or seasoning process evaporate and leave the compound in a hard condition. The solid solvents possess so little volatility that they practically remain in the final product combined with the pyroxyline, and as they possess the power of dissolving pyroxyline when heated to their melting-points, the compounds made with them are plastic—that is, they can be molded into various shapes under heat and pressure. The solid solvent commonly used is camphor, which requires so high a degree of heat to melt it that unless it is associated with some portion of liquid solvent compounds made with it are only moldable at such high temperatures as to need great care in their manipulation.

It is the object of the present invention to enable the operator to employ camphor as a solvent, with the avoidance of the difficulties which have heretofore been incidental to its use, and at the same time produce these compounds at a lower cost.

My experience has shown that many substances, which, in view of their power of lowering the melting-point of camphor when mixed therewith, might be supposed to operate beneficially in pyroxyline combinations, have failed to form useful compounds with the camphor and pyroxyline, because of a weakening effect on the solvent or some other deleterious action on the combination. For instance, many substances which are colorless in themselves react with the pyroxyline to make a dark-colored or decomposed mass. A practical trial with numerous agents which promised good results in pyroxyline compounds has caused me to appreciate the delicate and changeable character of pyroxyline when it is combined with other substances.

The present invention enables the operator to avail himself of all the valuable properties of camphor in these compounds, and at the same time avoid the difficulties incident to its employment. This I accomplish by using in combination with the camphor the well-known crystalline substance naphthalene (naphtalin).

My invention is based upon the discovery that naphthalene, while not a solvent of pyroxyline in itself, forms a powerful solvent of pyroxyline when combined with camphor, preferably in equal proportion by weight, and that a compound composed of pyroxyline, camphor, and naphthalene, as hereinafter more fully described, is plastic at moderate temperatures.

As to the state of the art, the application of pyroxyline compounds, and the difficulties connected with the discovery of suitable solvents, I refer to my United States Patent No. 517,987, dated April 10, 1894.

In making the present compound, I prefer to proceed in the usual well known-manner of making solid pyroxyline compounds, which

involves grinding the solid solvent and pyroxyline together while in a hydrated condition, next removing the water by suitable means, and then adding a sufficient quantity of liquid solvent to allow the mixing to be completed, or the conversion into a solid homogeneous mass effected by means of masticating-rolls and subsequent solidification in stuffing machinery or presses or dies.

I have found during my experiments in this field that while naphthalene is difficultly soluble in some of the ordinary liquid menstrua employed in making these compounds, it is easily dissolved in these menstrua in the presence of camphor. Thus, while naphthalene requires for solution without camphor in the following liquids about the proportions specified,—viz: ninety-five per cent. grain alcohol, ten to eleven parts; absolute alcohol, eight parts; wood spirit, six to seven parts; acetate of amyl for manufacturing purposes, two to two and a half parts—on the other hand a mass of undissolved naphthalene and wood alcohol becomes a clear solution when camphor is added to the mixture. A mixture of three parts of camphor and two parts naphthalene is soluble in about three and one-fourth parts ninety-five per cent. grain alcohol, two parts absolute alcohol, one and four-tenths parts wood spirit or one-half part acetate of amyl for manufacturing purposes. All these proportions are for the ordinary temperature of the workroom. I use by preference a refined grade of wood spirit.

My new compound when in a solid or liquid condition can be seasoned or dried by the evaporating of the wood alcohol or other volatile solvent, according to the usual method, and as distinguished from the pyroxyline-camphor compounds made with wood alcohol or other solvent. The compound can be thoroughly deprived of all wood alcohol or other solvent without impairment of its plasticity.

In forming a product which is easily plastic at temperatures below the boiling-point of water I usually employ the following proportions: Four parts soluble pyroxyline, one part camphor, one part naphthalene, and a sufficient quantity of wood spirit. The dried product of this mixture is plastic, as before described, at low temperatures. Sheets made from it can be easily bent or stretched into shape in hot water, or, say, at about 70° to 80° centigrade, or even lower temperatures, especially when the camphor is slightly in excess of the naphthalene. When I desire less plasticity I prefer to decrease the amount or proportion of naphthalene, and at the same time increase the proportion of camphor, so that the proportion of the total solid solvents will constitute about two parts to each four parts of pyroxyline, though of course it is understood that by decreasing the proportion of solid solvents to the pyroxyline I can also reduce the plasticity. Although the solvent composed of naphthalene and camphor is still active when the proportion of naphthalene is double that of the camphor I prefer usually to employ about equal parts of each. In using an excess of naphthalene I advise the operator to employ a pyroxyline having the solubility which is best fitted for the weakened solvent action. I also find that as the proportion of naphthalene is increased beyond that of the camphor, there is a corresponding decrease in the plasticity. In other words, any large increase in the proportion of camphor acts to make a material more resistant to molding or working by heat and pressure, and any increase in the naphthalene acts in the same way, but to a less degree. The increase of naphthalene also weakens the plastic property, and if carried too far the beneficial effects of the camphor-naphthalene combination are lost.

In my various experiments with naphthalene as an ingredient in pyroxyline compounds I have paid particular attention to the attempt to obviate or minimize its obnoxious odor, and after many experiments I finally discovered that when a sufficiently-pure naphthalene was employed it gave off very little smell in the final thoroughly-dried product, the odor being most perceptible when the liquid solvent was evaporating. Hence the product when it reaches the market, is not objectionable on account of odor; but, to produce the best results, I combine with my mixture a small percentage of some volatile oil or odoriferous principle, such as the heavy ethers used in perfumery and flavorings, so as to substitute a pleasing odor for the trace of naphthalene which might be detected in these materials. In this connection the liquid solvents recommended in several of my prior patents, especially my United States Patents Nos. 269,340, 269,341, 269,344, and 269,345, can be employed, in which case the solvent action will not be interfered with, but rather aided by means of these useful menstrua. The proportion or kind of odoriferous substance to be used will depend on the strength or persistency of its odor and the individual taste of the operator or user of the goods. As an oil I recommend oil of cassia. As colorless ethers I recommend such substances as acetate of amyl or salicylate of methyl, in the proportion of, say about one or two per cent. to the amount of pyroxyline, although, for the reasons given, these are only approximate proportions and can be varied.

It is evident that, regardless of the process by which the final dried compound of pyroxyline, camphor, and naphthaline, with or without other modifying substances, is produced, (whether by evaporating down liquid solutions or the stiffer masses formed in rolls or mixing-machinery,) the flowing or change of shape under heat or heat and pressure of the dried compound is due to the solvent action of the camphor-naphthaline mixture. The presence of some liquid solvent, especially

such proportion of liquid as is insufficient in itself to give plasticity to the product, does not matter.

I find that, contrary to the inferences drawn from the known lack of harmony between naphthalene and the usual liquid solvents by which we might expect it to separate from the solvent and pyroxyline during the evaporating down of the compound to produce a film or sheet, the use of the mixture of naphthaline and camphor in suitable proportion—say one part of the mixture to each two parts of the pyroxyline—forms a useful solid solvent in liquid compounds, and, for instance, where acetone is employed as the liquid solvent I am enabled to produce a perfectly clear solid film or sheet free from the blemishes which often accompany the employment of this liquid process.

The camphor-naphthalene solvent can be employed in all the compounds of this class, and in combination with any of the solvents used by the operator, according to the result he wishes to obtain, and also in varying proportions.

It is evident, also, that I am not confined to any particular process for effecting the combination of solid solvent and pyroxyline. For instance, the camphor-naphthalene solvent can be dissolved in the liquid menstruum or liquid menstrua employed, and then added to and intimately mixed with the pyroxyline in a manner which is equivalent to first combining it with the pyroxyline by means of grinding operations. Again, the liquid menstrua can be entirely dispensed with by using the process which involves intimately mixing the pyroxyline, camphor, and naphthalene in the presence of water, then drying out the water and subjecting the dry hard compound to heat and pressure in order to bring into action the active or converting power of the solvent, and thus form a homogeneous mass in the dry way, or any other equivalent method can be employed.

The terms "heat" and "pressure" as used by me include the manipulation of these materials in heated rolls, (whether the heat comes from steam or friction during the mixing operation,) the heating of the compound in dies under pressure, or the heating or bending or twisting of these materials in hot water.

I am aware that naphthalene has been used in the household and for medicinal and other purposes as a substitute for camphor, and that it has received such designations as "naphthalene-camphor" and a "substitute for camphor" by reason of such use.

I believe that I am the first to make a mixture of camphor, naphthalene, and pyroxyline and subject such mixture to the action of heat, by means of which the solvent action of the camphor and naphthalene is brought into play so as to obtain useful results in this art.

Having thus described the object and nature of my invention, what I claim, and desire to secure by Letters Patent, is—

1. The process of manufacturing compounds of pyroxyline which consists in intimately mixing pyroxyline, camphor and napththalene, and subjecting the resulting compound to heat and pressure, substantially as set forth.

2. The process of forming compounds of pyroxyline which consists in mixing pyroxyline, camphor, naphthalene and a liquid menstruum, or liquid menstrua, and then subjecting the resulting compound to heat and pressure, substantially as set forth.

3. The process for the manufacture of compounds of pyroxyline which consists of the following steps: first, intimately mixing pyroxyline, camphor, naphthalene and a liquid menstruum or liquid menstrua; second, drying out the liquid menstruum or liquid menstrua; third, subjecting the dry compound to heat and pressure.

4. As a new composition of matter, a pyroxyline compound consisting of pyroxyline, camphor and naphthalene, substantially as described.

5. As a new composition of matter, a pyroxyline compound consisting of pyroxyline, camphor, naphthalene, and a liquid menstruum or liquid menstrua, substantially as described.

JOHN H. STEVENS.

In presence of—
THEO. M. SAMMIS,
GEORGE C. GILLMORE.

Correction in Letters Patent No. 543,197.

It is hereby certified that the assignee in Letters Patent No. 543,197, granted July 23, 1895, upon the application of John H. Stevens, of Newark, New Jersey, for an improvement in "Compounds of Pyroxylin," should have been described and specified as *the Celluloid Company, of New York, N. Y., a corporation of New Jersey*, instead of the "Celluloid Company, of New York, N. Y.;" and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed, countersigned, and sealed this 30th day of July, A. D. 1895.

[SEAL.]

JNO. M. REYNOLDS,
Assistant Secretary of the Interior.

Countersigned:

JOHN S. SEYMOUR,
Commissioner of Patents.