UNITED STATES PATENT OFFICE.

JOHN H. STEVENS, OF NEWARK, NEW JERSEY, ASSIGNOR, BY MESNE ASSIGNMENTS, TO THE CELLULOID COMPANY, OF SAME PLACE.

MANUFACTURE OF SOLID OR MASSIVE COMPOUNDS OF PYROXYLINE.

SPECIFICATION forming part of Letters Patent No. 543,108, dated July 23, 1895.

Application filed June 9, 1890. Serial No. 354,785. (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 the Manufacture of Solid or Massive Compounds of Pyroxyline, of which improvement the following is a specification.

This invention relates to the manufacture or manipulation of those varieties of material designated as "solid" or "massive" compounds of pyroxyline, or those compounds in which the process of conversion is effected while the material is in a solid or massive condition, which, as is well known, have already been the subject of extensive investigation and numerous patents, and it has for its object the production of a new composition of matter by bringing together into new relations, and with novel effects, certain substances well known in chemistry, as hereinafter described.

The special variety of pyroxyline compounds to which this invention relates is the one employed in the arts as an imitation of various natural substances. It is distinguished from the solid explosive compounds not only by the difference in solubility of the pyroxyline employed, but by the widely-different characteristics and uses of the present compound and the explosive compositions, one being valuable by reason of its stable nature, plasticity, solidity, color effects, and susceptibility, and to artistic and mechanical manipulations, while the other generally possesses none of these qualities, but its special value is due to its loosely-held components, which are brought together and associated for the express purpose of forming a compound instantaneously resolvable into gases, the valuable properties of explosives being only exhibited at the moment of disorganization.

The state of the art and the properties and uses of the pyroxyline compounds to which this invention relates are set forth in the United States Letters Patent granted to me on April 10, 1894, No. 517,987, which was granted to me on application therefor filed simultaneously with the application for the present patent.

The distinctive novelty of this present improvement in the art or manufacture consists in the employment, in combination with pyroxyline, of the solid substances known as "dinitro-toluol," in such a manner that the presence of dinitro-toluol gives the property of plasticity to the compound and renders it susceptible of conversion into an amorphous condition, or permits its manipulation or change of shape by the ordinary means employed in connection with other solid pyroxyline compounds, and in addition furnishes a compound possessing entirely new and unique properties.

My invention is based upon the fact that dinitro-toluol, when melted by heat, is an active solvent of "soluble pyroxyline," and that it is especially applicable, not only as a solvent when heated, but also by reason of the peculiar properties of its combination with pyroxyline in this particular class of compounds, the discovery of which facts I believe to be entirely original with me.

The difficulties connected with the discovery and application of pyroxyline solvents suitable for practical use are mentioned in Patent No. 517,987, before referred to.

In combining dinitro-toluol with pyroxyline I form a compound possessing many of the advantages over the well-known camphor-pyroxyline compounds which I have secured in the acetanilid-pyroxyline compound, and as described in my Patent No. 517,987, already referred to.

The dinitro-toluol differs from the phenylacetamide (acetanilid) by possessing more odor and color and the power of forming a pyroxyline compound which is more plastic under heat or more easily manipulated at elevated temperatures than the phenylacetamide (acetanilid) combinations. Otherwise the description of the phenylacetamide (acetanilid) and its compounds with pyroxyline in Patent No. 517,987 will apply to the dinitro-toluol and its pyroxyline compounds.

In making the combinations with dinitro-toluol I also prefer the processes described in Patent No. 517,987. This present invention can also be used with excellent results in connection with the phenylacetamide (acetanilid) of Patent No. 517,987, by using a mixture of dinitro-toluol and phenylacetamide (acetani-

lid) as the solid solvent. The proportions between the two substances can be varied at will, and compounds of different degrees of susceptibility to heat, when molded or manipulated, can be thus produced. An excess of the dinitro-toluol gives more plasticity than an excess of the phenylacetamide (acetanilid), and the proportion of the mixed solvent can be about the same as that recommended for either the dinitro-toluol or the phenylacetamide (acetanilid) alone.

In using camphor it has been customary to use mainly ethylic or methylic alcohols, although to a less extent other liquids have been used. I have found that dinitro-toluol is quite distinct from camphor in its solubility, and the use of ethylic and methylic alcohols in connection with it is not as practicable as when they are employed with camphor. This arises from the fact that dinitro-toluol is almost insoluble in grain alcohol, (ethylic alcohol). Even one hundred parts of such alcohol does not seem to dissolve it. It is more soluble in methylic alcohol, (wood spirits,) about ten parts of such alcohol appearing to dissolve one part of the dinitro-toluol. I prefer and recommend acetone as the liquid agent in my present compound because it has been found to be a superior menstruum for the dinitro-toluol. After various experiments I have ascertained that dinitro-toluol is readily soluble in a small portion or about one and one-half parts of acetone. All of these solubilities just given are at the ordinary temperature of the atmosphere. This solvent power of the acetone enables me to use it with great success in making pyroxyline compounds where a liquid solvent is required to be employed, and I obtain a result impossible with either ethylic or methylic alcohols. I have made this employment of acetone the subject of another application, to be filed simultaneously herewith, Serial No. 354,787, and designated as "Case D." I would say, however, that both the ethylic and the methylic alcohols mentioned can be employed in connection with dinitro-toluol in these solid compounds, and they may be rendered quite efficient by simply heating the receptacle containing the mixture of pyroxyline, dinitro-toluol, and either of the alcohols just mentioned to a sufficiently high temperature to cause it to cohere or to bring it to a dough-like state. This heating of the compound in a closed receptacle is similar in the reasons therefor and the effect of the heating to the operation recommended in my Patent No. 269,342, of December 19, 1882, where I refer to the mixture of pyroxyline, dinitro-benzene, and alcohol. After this treatment the combination will be in a condition suitable for mastication in heated rolls. These precautions are unnecessary when acetone is employed, for the reason above given.

I refer to the descriptions in Patent No. 517,987 as to the solvent action of the phenylacetamide (acetanilid) on the pyroxyline when it is heated in connection therewith, even in the presence of a small proportion of liquid solvent, insufficient in itself to cause the compound to flow or change its shape; also, to the solvent action of the phenylacetamide (acetanilid) under heat when the combination of solid solvent and pyroxyline is in a converted or homogeneous condition, regardless of the process which brought it to that state. I make the same claim with regard to the solvent action of the dinitro-toluol, as I mean to be distinctly understood as claiming that, even in the presence of the small proportion of liquid solvent, the dinitro-toluol would be acting as a pyroxyline solvent when subjected to heat and pressure.

My dinitro-toluol-pyroxyline compounds, whether made by simply combining dinitro-toluol and pyroxyline, or formed with the aid of liquid solvents in heated rolls, or by dissolving the pyroxyline in a liquid solution of dinitro-toluol, or in any equivalent manner, when in a dry or seasoned condition or a comparatively hard state, due to the absence or removal of sufficient liquid to soften it, is in such a condition that when it is subjected to heat and pressure it depends for its plastic property or susceptibility of being flowed under heat and pressure upon the solvent powers of the dinitro-toluol, and therefore any such heating or the production of these conditions or effects is an employment of the dinitro-toluol, made efficient by heat, as a solvent of pyroxyline. As to proportions, the dinitro-toluol can be used in smaller proportions than the phenylacetamide (acetanilid) of Patent No. 517,987. This is on account of its superior plastic effects. I would recommend, however, about the same proportions and limitations as are described for the phenylacetamide (acetanilid) in Patent No. 517,987.

In making a compound without the use of liquid solvents good proportions are: one hundred parts by weight of pyroxyline and fifty parts of dinitro-toluol and *quantum sufficit* of any pigment or coloring matter, as desired.

If the ingredients of the above mixture have been intimately combined with sufficient care, and thoroughly freed from adherent moisture they can be converted into a solid homogeneous mass by subjecting the mixture to pressure (say of one thousand pounds to the square inch) and heated to about the melting-point of the dinitro-toluol employed, (usually from 160° to 170° Fahrenheit.) The compound, however, under these conditions is so stiff, or flows so slowly under heat, that it is best to operate on small masses at a time, and also to have the shape of the pressed pulp conform, as closely as possible, to the final shape desired in the solid converted product. The operation requires great care, for no one part of the mass must be overheated while waiting to have the heat penetrate the other parts, it being well known that a uniform temperature

is difficult to obtain in molding operations, and this is the reason why I recommend the working of small masses, in which case the temperature can be controlled with more certainty. The material, when converted, can afterward be molded into articles with less trouble than is required to convert the original product, as the converted mass is in much better condition for remolding, the pyroxyline having been acted upon and combined with the solid solvent.

The inflammable nature of pyroxyline, especially when heated in an uncombined condition, must also be taken into account by the operator when applying heat to the mass before conversion has been effected. To facilitate the union of the different ingredients of the compound, it is best to subject the wet pulp, from which the product is originally made, to enormous pressure while it is being dried. This, by compacting the ingredients, renders their conversion a simpler operation.

In obtaining a solid product without the aid of liquid solvent the operation must be performed by one having a thorough knowledge of pyroxyline and its action under heat and pressure, and the above instructions should be carefully observed. In every case, also, the die or mold or other apparatus used should be arranged so that the compound is not entirely excluded from the atmosphere, so that in case a careless preparation of the ingredients or careless manipulation by the operator should produce a burning of the materials the released gases will find a ready outlet and the decomposition of the material would be discovered in time. This can be done by having the parts of the apparatus fit loosely. For instance, where a die is used the plunger can have a space of, say, one-eighth of an inch around it. These precautions are not necessary with a carefully-prepared material after it has been converted into a solid compound suitable for subsequent remolding, as above described, for the thoroughly-converted product made by this process simply resembles what is ordinarily recognized as a well-seasoned compound of pyroxyline, and can be treated as such. Where, however, the dinitro-toluol is employed in conjunction with liquid solvents, I recommend the following method of manufacture: The dried cake produced by pressing the wet pulp containing the dinitro-toluol and coloring materials between blotting-papers is to be broken in small pieces, and if it is desired to use a comparatively small proportion of liquid solvent, simple or compound, such liquid is then mixed in proportion of from forty parts to fifty parts to each one hundred parts pyroxyline present. For this purpose I prefer to use acetone as the liquid, as already explained. This mixture is allowed to stand in an air-tight vessel for several hours in order to allow the acetone to become fairly well diffused throughout the mass. After this is done the mixture is ready for mastication, which is performed in heated rollers at a temperature of 120° Fahrenheit, as is customary in manufacturing such pyroxyline compounds as this patent relates to. After this operation is proceeded with far enough, as is well understood, the material is removed from the rollers and receives subsequent treatment in so-called "stuffing machinery" or presses in order to solidify it and form it into various shapes—such as tubes, rods, and blocks—from which sheets can be cut, as is understood and more particularly described in my Patent No. 517,987.

Among the advantages I claim for this new compound of pyroxyline, of which dinitro-toluol is the solvent, are that the operations of mixing are carried on without the loss by evaporation incident to the use of camphor, thus permitting a freer use of drying methods and relieving the work-room from the camphor fumes. There is practically no loss of the solid solvent by evaporation, and the liquids can be entirely removed from the compound without impairing its plasticity when heated at fairly-low temperatures. Many difficulties, more or less connected with or due to the continual warping of the older materials containing camphor, will be remedied by the application of my new compound to such cases. I would mention drawing instruments, parts of machinery, and articles requiring to be nicely fitted together—like boxes, for example. My new compound will also be found much harder and more plastic than compounds made with camphor. When used alone as a solvent, of course it is limited to what is known as the "solid" or "plastic" process of conversion; but this process may also be practiced, as above shown, by adding such small quantities of liquid solvents as will not make the compound flow or result in what is known as the "fluid" process of conversion. I have filed a separate simultaneous application, Serial No. 354,787, and designated as "Case D," for the use of this ingredient in the fluid process of conversion, because special means are often required to render it effective in the fluid compounds and to prevent it from injuring them by its presence, means of remedying which I have specified and claimed in several other applications, and the use of the ingredient in the solid or plastic process is therefore to be definitely distinguished. As the result of numerous experiments I have demonstrated its extraordinary utility in the solid varieties, as herein described, and the novelty of my present invention depends on such demonstration, according to the principles hereinbefore set forth or referred to.

I wish it distinctly understood that even if pyroxyline is treated by the liquid mode of conversion and the liquid is then evaporated and then dinitro-toluol be present in proportions such as to produce, after evaporation of the liquid solvents, what is substantially a compound of pyroxyline and dinitro-toluol, any heating or treatment of the result-

ing solid which will develop the latent solvent power of the dinitro-toluol, so that it will soften, dissolve, or make plastic the pyroxyline, is a use of the solvent powers of the dinitro-toluol, as already explained, and such operation is within the invention herein set forth.

The use of dinitro-toluol in solvent or massive compounds of pyroxyline is not incompatible with the employment of camphor. On the contrary, the use of dinitro-toluol in the camphor compounds imparts some of its properties to such compounds—namely, by enabling the camphor to melt at a much lower temperature by reason of its association therewith, and thus removing one of the objectionable features connected with the employment of camphor alone as a solid solvent. Consequently compounds containing this combined solvent can be more readily molded at safe temperatures without the necessary presence of a residue of the alcoholic or other liquid solvent, thus rendering the manipulation of the camphor compound more uniform and certain. In making such compound I grind together the camphor dinitro-toluol, pyroxyline, and other necessary ingredients, preferably in the presence of water and then dried in the regular manner. Ethylic and methylic alcohols or other suitable liquid may then be added to the mixture and the whole stirred together and left over night in an air-tight vessel. The resultant mass is masticated in rolls and formed into shapes in the usual well-known manner. Good proportions for this latter compound are, one hundred parts pyroxyline, forty parts camphor, ten parts dinitro-toluol, and about forty to forty-five parts of either of the alcohols mentioned, or acetone can be used in place of the alcohol. The respective proportions of camphor and dinitro-toluol can be varied at will. This camphor dinitro-toluol-pyroxyline compound has been separated from the present specification, and is made the subject of a separate application, Serial No. 494,298, where it will be found more particularly described.

What I claim, and desire to secure by Letters Patent, is—

1. The process of manufacturing pyroxyline compounds which consists in intimately mixing pyroxyline and di-nitro-toluol and subjecting such mixture to heat and pressure sufficient to render the compound plastic, substantially as described.

2. The process of manufacturing solid or massive pyroxyline compounds, which consists in mixing pyroxyline, di-nitro-toluol and a liquid menstruum or liquid menstrua and subsequently subjecting the resulting compound to heat and pressure sufficient to render the compound plastic, substantially as set forth.

3. The product resulting from the process of manufacturing the solid or massive pyroxyline compounds which consists in mixing pyroxyline and di-nitro-toluol and subsequently subjecting the resulting compound to heat and pressure sufficient to render the compound plastic, substantially as described.

4. The product resulting from the process of manufacturing solid or massive pyroxyline compounds, which consists in mixing pyroxyline, di-nitro-toluol and a liquid menstruum, or liquid menstrua, and subsequently subjecting the resulting compound to heat and pressure sufficient to render the compound plastic, substantially as described.

5. As a new composition of matter, a solid or massive pyroxyline compound, of the variety employed for imitating natural substances, containing pyroxyline and di-nitro-toluol, substantially as set forth.

In testimony whereof I affix my signature, in presence of two witnesses, this 2d day of June 1890.

JOHN H. STEVENS.

Witnesses:

WM. H. BERRIGAN, JR.,

JAMES J. COSGROVE.