UNITED STATES PATENT OFFICE.

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MANUFACTURE OF DERIVATIVES OF TOLUENE.

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To all whom it may concern:

Be it known that I, JULES MAIRE, residing at Argenteuil, France, have invented a new and useful Improvement in the Manufacture of Derivatives of Toluene, which is fully set forth in the following specification.

In recent years, it has been attempted to remedy the defects of gelatin explosives containing nitroglycerin, by substituting for the latter, either partly or wholly, various liquid nitro-compounds which are also solvents of nitro-cellulose, the chief object of this substitution being to obtain gelatins which freeze at a lower temperature than gelatin dynamites. More particularly, it has been proposed to use, for the purpose specified, liquid nitro-toluene compounds which recently appeared in the market under the name of "liquid trinitro-toluenes," but the gelatin explosives thus obtained have not fulfilled expectations, since, after having been stored for a certain time, they gradually harden and freeze more and more easily, this being due to the fact that the said liquid trinitro-toluenes are products which are not properly defined and are essentially variable not only if obtained from different factories, but also if obtained at different times from the same factory. These liquid trinitro-toluenes vary materially as regards the proportion of nitrogen, (from 14.5 to 15.8 per cent.), and the freezing point, (from —5° C. to —20° C.). They remain in a state of very pronounced superfusion for several weeks after their manufacture, then become muddy, thickened and changed in color. They all have a more or less pronounced smell of mononitro-toluene, and lose a considerable fraction of their weight after having been heated for a short time to 60° C., (from 2 to 2.5 per cent. at the end of twenty-four hours). During heating, they precipitate more or less considerable quantities of solid matter. It follows, therefrom, that gelatin explosives manufactured with these pseudo-liquids, are completely modified after having been heated; that is to say, they lose their plasticity and become hardened, while the smell is not changed. Also it may be pointed out, in passing, that this partial volatilization, shown and accelerated by the heating, necessarily takes place at the ordinary temperature in the course of time, so that the aforesaid compounds are obviously, therefore, merely by-products of undetermined composition, obtained by chance in the course of manufacture, in which the subsequent addition of liquid mononitro-toluene enables the solid trinitro-toluene to be artificially dissolved, so as to increase the proportion of nitrogen. The spontaneous volatilization of the mononitro-toluene, which is inevitable in the course of time, results, as has been shown, in the crystallization of the solid products which are dissolved by its means, and thus also readily explains the progressive hardening of the gelatin explosives obtained with these pseudo-liquids, during their storage. Moreover, this hardening is unavoidable after a lapse of a few weeks, even in a closed vessel, owing to the spontaneous cessation of the state of superfusion which characterizes these pseudo-liquids.

This invention relates to the systematic manufacture of new supernitrated compounds of toluene which, on the contrary, are true liquids, inasmuch as they have sharply defined melting points which can be accurately determined almost within 1°, and if they are cooled, they no longer precipitate solid material but are entirely frozen. They are all odorless, and lose only a very small proportion of their weight when heated to 60° C., their properties continuing unmodified after such heating, and the compounds themselves remaining as clear as ever. Gelatin explosives manufactured with these liquids do not show any change in plasticity after heating, but remain plastic no matter how long they may be stored.

An entire series of liquid nitro-toluenes complying with the different conditions and containing proportions of nitrogen between 15.3 and 16 per cent., and melting between the ordinary temperature and —20° C. can be obtained in accordance by the methods hereinafter described.

Up to the present time, generally speaking, all nitro-toluenes, whether simple or complex, solid or pseudo-liquid, having a degree of nitration greater than that of mononitro-toluene, have been obtained by starting operations either with para-mononitro-toluene alone, or with ortho-mononitro-toluene alone, or with a more or less defined mixture of both and meta-mono-

nitro-toluene, in which the proportion of ortho-mononitro-toluene always considerably exceeded 50 per cent., while that of para-mononitro-toluene did not exceed 40 per cent., and that of meta-mononitro-toluene was, at the outside, 2 per cent.

It has been found that in order to obtain any of the true liquid compounds belonging to the class defined in the foregoing and having the properties described, it is necessary and sufficient to use a mixture of mononitro-toluenes in which, contrary to what has heretofore been done, the proportion of meta-mononitro-toluene is always very considerable and varies between a minimum of 45 per cent., and a maximum of 85 per cent., the remainder being constituted either by ortho-mononitro-toluene, or by para-mononitro-toluenes in which, contrary to what using smaller proportions of meta-mononitro-toluene than the said minimum, or greater than the said maximum, only solid or pasty products are obtained.

Liquid compounds which are exactly binitrated and which form what will be called Series I, are obtained by mixing with the usual nitrating mixtures of sulfuric and nitric acids, mixtures of mononitro-toluenes constituted in accordance with the principle above referred to. They are also obtained by mixing with the desired quantity of binitro-toluene obtained by the nitration of meta-mononitro-toluene, suitable quantities of binitro-toluenes obtained by nitration either of ortho-mononitro-toluene alone, or of para-mononitro-toluene alone, or of a mixture of both, the transformation of the mixture of mononitro-toluenes into binitro-toluenes being effected with the aid of any of the nitrating mixtures generally used for this operation.

Supernitrated liquid compounds, forming what may be called Series II, are obtained in turn by any of the following methods, the first and simplest of which consists in dissolving one of liquid binitro-toluenes of Series I, in a definite quantity of pure solid trinitro-toluene, (melting point 82° C.), or of commercially solid trinitro-toluene (melting point from 70 to 72° C.). The second method consists in nitrating with the usual nitrating mixtures, binitro-toluenes of Series I, and then dissolving a definite quantity of the trinitro-toluenes thus obtained in any one of the liquid binitro-toluenes of Series I. The third method, which is more complicated consists in subjecting to the action of the usual nitrating mixtures, a mixture of given proportions of solid trinitro-toluene with meta-mononitro-toluene, to which latter have been previously added dissolved quantities of either ortho-mononitro-toluene or para-mononitro-toluene, or both, as previously stated. (It is obvious that in the latter case the trinitro-derivative does not take part in the nitration, and that at the moment of the usual washing terminating the operation, there is a risk of a portion of the same being dissolved in the washing water to the detriment of the final proportion of nitrogen.) It is also possible, as a fourth method, to subject the mixture in desired proportions of meta-mononitro-toluene and either the ortho-mononitro-toluene or para-mononitro-toluene, or both, to the nitrating action of such a quantity of the nitrating mixture, and in such conditions of temperature, as to produce at once not only binitro-toluene, but, also, the desired proportion of binitro-toluene, in order to obtain the desired supernitrated derivatives in liquid form. This method is, however, more difficult than the preceding ones, as it requires a higher temperature for the nitration, and the yield is less good, owing to unavoidable losses by oxidation. It is obvious that it would be also possible to employ other more or less indirect methods, but in all of these cases, the common and indispensable feature, is, as may be seen, the use at the beginning of the operation or operations, of a very considerable proportion of meta-mononitro-toluene combined with the use, equally imperative, of large quantities of ortho-mononitro-toluene, or of para-mononitro-toluene, or of a mixture of both, the proportion of the meta-mononitro-toluene which must remain between 45 and 85 per cent. of the whole, varying according to the method adopted and according to the liquid compound to be obtained.

Examples of the relative proportions of the different ingredients used in various cases for obtaining given liquid compounds are given below:

(1) Production of liquid derivatives exactly binitrated, (Series I).

(*a*) Use of meta-mononitro-toluene with ortho-mononitro-toluene alone.

Meta-mononitro-toluene.	Ortho-mononitro-toluene.	Freezing point.	Order No.
Parts. 80	*Parts.* 20	Solid at the ordinary temperature.	1
70	30	−2.5° to −4°.	2
60	40	−2° to −3°.	3
50	50	0°.	4
45	55	Solid at the ordinary temperature.	5

(*b*) Use of the meta-mononitro-toluene and of the para-mononitro-toluene.

Meta-mononitro-toluene.	Para-mononitro-toluene.	Freezing point.
Parts. 85	*Parts.* 15	Solid at ordinary temperatures.
80	20	−2°.
70	30	−6°.
65	35	Solid at ordinary temperatures.

(*c*) Use of the meta-mononitro-toluene

and ortho-mononitro-toluene and para-mononitro-toluene.

Meta-mononitro-toluene.	Ortho-mononitro-toluene.	Para-mononitro-toluene.	Freezing point.
Parts.	*Parts.*	*Parts.*	
50	45	5	−3°.
50	35	15	27°.
60	36	4	Muddy, very thick.
60	24	16	Do.
60	4	36	25°.
80	2	18	Half solid, half liquid.
80	6	14	−1° to −2°.
80	10	10	−1° to −2°.
80	12	8	−1° to −2°.
80	14	6	−1°.
90	18	2	0°.

2. Production of supernitrated liquid derivatives; that is to say, those with the proportion of nitrogen comprised between 15.3 and 16 per cent., (Series II).

(*a*) Dissolving solid trinitro-toluene in liquid binitro-toluenes of Series I. (The solid trinitro-toluene used is the commercial product melting at from 72° to 74° C. The results are the same with para-trinitro-toluene melting at 82° C.).

Order No. of binitro-toluene Series I.	Quantity of binitro-toluene of Series I.	Quantity of binitro-toluene.	Proportion of nitrogen.	Melting point.
	Parts.	*Parts.*	*Per cent.*	
1.....	95	5	15.5	−4°.
	85	15	15.8	−11°.
	75	25	16.0	−24°; becomes muddy about −18°.
	70	30	16.2	Solid at ordinary temperature.
2.....	95	5	15.5	−5°.
	85	15	15.8	−13°.
	75	25	16.0	−23°; becomes muddy about −20°.
	70	30	16.2	Solid at ordinary temperature.
3.....	95	5	15.5	−6°.
	85	15	15.8	−13° to −14°.
	80	20	15.9	−17° to −18°.
	75	25	16.0	−26°; becomes muddy about −10°.
	70	30	16.2	Solid at ordinary temperatures.
4.....	95	5	15.5	−8°.
	85	15	15.8	−8°.
	75	25	16.0	Has no sharply defined melting point; becomes muddy about −5°.
	70	30	16.2	Solid at ordinary temperature.
5.....	95	5	15.5	Half solid, half liquid.
	85	15	15.8	Uncertain: melting point not sharply defined, becomes muddy about 5°.
	75	25	16.0	Do.
	70	30	16.2	Solid at ordinary temperature.

(*b*) Nitration of Series I, then dissolving the product thus obtained.

This method is not described herein, for the reason that it is more complicated than the preceding one.

(*c*) Direct nitration, by means of the ordinary nitrating mixture, of a mixture of meta-mononitro-toluene and of solid trinitro-toluene with either ortho-mononitro-toluene, or with para-mononitro-toluene, or with a mixture of both. Only one example will be given, owing to the complexity of this method. As a starting point is taken a mixture of 60 parts of meta-mononitro-toluene and of 40 parts of ortho-mononitro-toluene, for example, No. 3 of the Series I, and in the same is dissolved commercial trinitro-toluene. Mixture No. 3 of meta-mononitro-toluene and ortho-mononitro-toluene, 77 parts; trinitro-toluene, 23 parts; proportion of nitrogen after nitration, 15.8%; freezing point, —16° to —17°.

(*d*) Nitration, by means of a greater quantity of nitrating mixture, with heating to 90°, of a mixture of meta-mononitro-toluene or either ortho-mononitro-toluene, or with para-mononitro-toluene, or both.

It is possible to use, for instance a mixture of 60 parts of meta-mononitro-toluene and 40 parts of ortho-mononitro-toluene, and to nitrate the same with one and a half the quantity of nitrating mixture that would have been necessary for obtaining the exactly binitrated product. The first stage of nitration is carried out at a temperature of 60°, then it is raised to 90° and maintained for an hour to an hour and a half. The product obtained, after washing and neutralization, is liquid. Its proportion of nitrogen is 15.9%, its freezing point is —18°, and it has the same properties as those prepared in accordance with (*b*).

The new products obtained according to this invention can be used for any purposes in which the so-called commercial "liquid trinitro-toluene", is used, and they are especially well adapted for the manufacture of explosives.

I claim:—

1. The process of producing liquid nitro-toluene compounds which consists in nitrating an initial mixture of mononitro-toluenes containing essentially from 45 to 85 per cent. of meta-mononitro-toluene.

2. The process of producing liquid nitro-toluene compounds which consists in nitrating a mixture of mononitro-toluenes containing esentially from 45 to 85 per cent. of meta-mononitro-toluene, to obtain a liquid binitro-toluene; and dissolving in said binitro-toluene solid trinitro-toluene.

3. The process of producing liquid nitro-toluene compounds which consists in nitrating a mixture of mononitro-toluenes containing essentially from 45 to 85 per cent. of meta-mononitro-toluene to obtain a liquid binitro-toluene; nitrating said binitro-toluene; and mixing the resultant trinitro-toluene with liquid binitro-toluene.

4. The liquid nitro-toluene compounds obtained by nitrating mixtures of mononitro-toluene containing essentially from 45 to 85 per cent. of meta-mononitro-toluene, said compounds being true liquids having sharply-defined, constant melting points and characterized by their freedom from mono-

nitro-derivatives and from loss of weight when heated for a period of twenty-four hours to 60° C., and by the quantity of nitrogen which they contain remaining the same before and after such heating.

In testimony whereof I have signed this specification in the presence of two subscribing witnesses.

JULES MAIRE.

Witnesses:
EMILE LEDRET,
LUCIEN MEMMINGER.