

UNITED STATES PATENT OFFICE.

OSWALD SILBERRAD, OF BUCKHURST HILL, ENGLAND.

EXPLOSIVE.

1,092,758.

Specification of Letters Patent.

Patented Apr. 7, 1914.

No Drawing.

Application filed June 3, 1912. Serial No. 701,242.

To all whom it may concern:

Be it known that I, OSWALD SILBERRAD, Ph. D., a subject of the King of Great Britain and Ireland, director of the Silber-
rad Research Laboratories, and residing at
Buckhurst Hill, in the county of Essex,
England, have invented certain new and
useful Improvements in Explosives, of
which the following is a specification.

This invention relates to the preparation,
purification and use of nitro compounds and
particularly to the preparation, purification
and use of difficultly volatile nitrated prod-
ucts which remain liquid at ordinary tem-
peratures.

I have found that the neutral liquid por-
tion from the middle, heavy and anthracene
oils obtained from tar after suitable chemi-
cal washing produce on nitration under
suitable conditions a mixture of nitro com-
pounds, possessed of very low vapor ten-
sion and which remain liquid at ordinary
temperatures.

According to this invention therefore, in
the first place such an oily nitration product
is produced by subjecting a coal-tar product
of the kind referred to to nitration under
suitable conditions. Such a nitration prod-
uct can be produced from any or all or any
liquid neutral fraction of the following tar
products:—viz., the oils boiling between
about 200° to about 350° C., that is to say,
the liquid portions of middle, heavy and an-
thracene oils, the residues from the manu-
facture of carbolic acid, cresol, naphthalene
and anthracene and also coal tar lubricating
oil. In this connection I find that the high-
est fractions—i. e. the portion boiling from
about 270° C. to about 350° C.—do not so
readily lend themselves to the treatment
herein described, so that I prefer to utilize
oils of which at least the greater portion
boils from 200°–270° C.

The desired fraction or fractions is or are
freed, if necessary, from phenolic bodies,
bases and objectionable impurities, if any
by washing with alkali and acid in the usual
manner and in this way obtaining the neu-
tral portion, the degree of importance of
this chemical washing varying with the na-
ture and purity of the product required and
of the fraction of tar oil to be dealt with.

In order to effect nitration the tar oil as
aforesaid, after having been submitted to
such chemical washing as is desirable in the
usual manner, is run into a nitrating vessel

fitted with an efficient stirring apparatus
and suitable cooling coils or jacket, and
brought into a state of violent agitation.
The desired amount of nitric acid is slowly
run in, the temperature being carefully con-
trolled by circulating water through the
coils or jacket, the mixture being violently
agitated the entire time. After the full
complement of nitric acid has been added
sulfuric acid sufficient to cause the comple-
tion of the reaction is run in, very special
attention being directed to the efficiency of
the agitation and to the control of the tem-
perature throughout the whole operation.
The mixture is then allowed to stand over
night, the oil separated, and washed with
water and dilute sodium carbonate in the
usual manner. I find that the usual method
of nitrating with mixed acids does not so
readily lend itself to this operation, so that
I prefer to employ the improved method
above indicated according to which I ob-
tain a mixture of the nitric acid and oil be-
fore adding the sulfuric acid. This is es-
pecially the case with regard to some frac-
tions. This method of nitration may with
advantage be applied to the nitration of hy-
drocarbons generally which give difficulties
in nitration by the usual methods.

In obtaining the oily nitration product
according to one example I charge a suit-
able still with creosote oil containing the
residue from the manufacture of carbolic
acid and naphthalene and collect that frac-
tion boiling from 200° to 270° C. After
freeing the distillate from any naphthalene
which separates out I subject it to chemical
washing with alkali and acid in the well-
known manner, using sufficient alkali to re-
move all phenolic bodies in the first place,
then water, then sulfuric acid, then dilute
alkali, and finally water again.

In effecting the washing I find it con-
venient to subject the oil to a thorough
washing with 2½% to 5% concentrated oil
of vitriol and to repeat this operation until
the desired degree of purity is obtained,
2.5% to 20% of acid being used in this
manner. After washing, the oil is again
distilled and the fraction boiling between
200° to 270° C. again collected, allowed to
stand and freed from any further quantity
of naphthalene which separates. The oil
is now ready for nitration, in order to effect
which I proceed as follows:—100 lbs. of oil
are run into a suitable nitrating vessel fitted

with agitator and cooling jacket. 68 lbs. of nitric acid (sp. gr. 1.50) are slowly run in and finally 88 lbs. sulfuric acid (sp. gr. 1.84) gradually added. During the whole operation the contents of the vessel are kept in violent agitation and the temperature is kept at 20° to 35° C. After the full complement of acid has been added, the mixture is allowed to stand for about 16 hours, the nitrated oil is separated from acid and washed with water and dilute soda carbonate in the usual manner. The product may be further purified if desired by distillation *in vacuo*, though this operation needs care; the vacuum should be maintained as high as possible, and the temperature should not be allowed to rise much above 240° C.

According to another method, the nitration may be carried out as follows: 1,000 parts by volume of oil, prepared as above boiling between 200° to 260° C. is run into a suitable nitration vessel fitted with agitator and cooling jacket. A mixture of 100 parts by volume of nitric acid of 1.5 sp. gr. with 25 parts of water is gradually run in. Then 100 parts by volume of nitric acid of sp. gr. 1.5 previously diluted with 10 parts of water are gradually added. Then 100 parts by volume of nitric acid 1.5 sp. gr. previously diluted with 5 parts of water are gradually added. Then 100 parts by volume of nitric acid of 1.5 sp. gr. are gradually added, and finally 150 parts by volume of nitric acid of 1.5 sp. gr. previously mixed with 450 parts by volume of concentrated sulfuric acid are gradually added. During the whole operation the contents of the vessel are kept under violent agitation and the temperature maintained preferably between 20° and 35° during addition of acid. The mixture is allowed to stand over night, and is then gradually warmed to 60° to 70° C. under stirring.

It should be clearly understood that I do not confine myself to the limits of the examples given above, but may obtain suitable liquid neutral portions of coal-tar boiling between about 200° to 350° C. in any desired manner irrespective of the manner in which said tar has been produced from coal, and may nitrate such products in any suitable manner and to any desired extent, such that the product of nitration is essentially a liquid. Broadly I find that the greater the quantity of nitric acid used, the more viscous will the finished product become.

In cases where very effective purification is required the following method may be adopted. The nitrated oil is first stirred with a weak solution say 5% of soda-ash, preferably at about 50° to 70° C. for a period of about 12 to 24 hours. It is then separated, washed with water, and run into

a suitable vessel containing clean water, preferably about 10 times its bulk, and also a few lumps of marble or the like are added, and the mixture gently boiled under the reflux condenser until all unstable compounds are decomposed. This is generally satisfactorily accomplished in from 24 to 48 hours.

Instead of soda-ash, I may use the carbonates or bicarbonates or hydrates of any of the alkali metals or mixtures containing any or all of these; similarly in place of marble I may use chalk, dolomite, magnesia or the carbonates or hydrates of any or all of the alkaline earths, or mixtures containing any of these or any difficultly soluble compound capable of neutralizing the nitrous acids, produced from the gradual decomposition of the unstable products with the production of bodies which are inert as regards the nitrated product.

Regarding the purification method above described it is to be observed that both it and its separate steps (*i. e.* the washing with soda-ash or other substance on the one hand or the digestion with a suspension of a carbonate, hydrate or other body on the other) are of general application in the treatment of nitro compounds requiring special purification.

When nitro derivatives of the higher boiling fractions of coal tar referred to are purified by the process, I find that the product is not only rendered stable, but undergoes other changes. Thus the viscosity is altered, and the tendency to solidify is lessened, while the quantity of solid produced in the event of solidification occurring is reduced.

In carrying the invention into effect according to another example, where, for instance, the impurity consists essentially of a nitroso body and the substance to be purified is required for the purpose of use in explosives, the nitro compound may be washed with water and run into a vessel containing clean water, preferably about ten times its bulk, and marble may be added and the mixture gently boiled under a reflux condenser until all unstable compounds are decomposed, the process occupying about 36 hours. Other insufficiently pure or mixed nitro compounds may be purified in a similar manner. The treatment is, therefore, of considerable importance when products are required for the manufacture of explosives, and especially of plastic explosives, as by means of the purification great stability, which is essential in such explosives, can be obtained.

By purification by means of carbonates or hydrates of the alkaline earths either with or without previous treatment with soda or the like I find that the heat test of the product is considerably raised, whereas purified in the ordinary manner, nitrated products produced according to the process

above described seldom show a heat test exceeding five minutes. Further, the tendency of the product to freeze and the consequent difficulty and danger of thawing is reduced.

The product or products of nitration of the coal tar fractions referred to are particularly suitable for use in the production of explosives and may be used for instance in blasting explosives either as the chief nitro compound therein or as a subsidiary ingredient. The fluidity of the nitro product referred to and its corresponding ability to render other nitro compounds either fluid or more fluid is an important factor in facilitating the incorporation of the ingredient and particularly in connection with the production of colloidal or plastic explosives.

Claims:

1. A process of preparing liquid difficultly volatile nitro derivatives from coal tar consisting in separating from coal tar a neutral liquid portion of the oils boiling between about 200° C. to 350° C. and nitrating the same by the action of nitric acid of suitable strength alone and then completing the nitration with nitric acid in the presence of sulfuric acid, as set forth.

2. A process of preparing liquid difficultly volatile nitro derivatives from coal tar consisting in separating from coal tar a neutral liquid portion of the oils boiling between about 200° to 350° C. and nitrating the same by the action of successive quantities of nitric acid of increasing strength, finally completing the nitration with nitric acid in the presence of sulfuric acid, as set forth.

3. A process of preparing liquid difficultly volatile nitro derivatives from coal tar, consisting in separating from coal tar a portion of the oils boiling between 200° C. and 350° C., freeing said portion from phenolic and basic bodies, and nitrating the neutral liquid portion of oils boiling between 200° C. and 350° C. so obtained by successive quantities of nitric acid of increasing strength, and completing the nitration with nitric acid in presence of sulfuric acid, as set forth.

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

OSWALD SILBERRAD.

Witnesses:

HERBERT D. JAMESON,
C. P. LIDDON.