# UNITED STATES PATENT OFFICE.

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## PROCESS OF NITRATING TOLUOLS CONTAINING PARAFFINS.

1,225,321. Specification of Letters Patent. Patented May 8, 1917.

No Drawing. Application filed March 23, 1916. Serial No. 86,180.

*To all whom it may concern:*

Be it known that I, BERNHARD JACQUES FLURSCHEIM, a subject of the King of England, residing at Fleet, county of Hampshire, England, have invented a new and useful Improvement in Processes of Nitrating Toluols Containing Paraffins, of which the following is a full, clear, and exact description.

The object of my invention is to nitrate toluol containing paraffins and more particularly to treat the mononitro derivative thereof in such manner as to separate therefrom the contained paraffins. The process is also applicable to other hydrocarbons of the benzol series and especially to the manufacture of dinitrobenzol.

The manufacture of trinitrotoluol from toluols containing paraffins has heretofore been carried out in the following way:

The toluol is nitrated to mononitrotoluol, the mononitrotoluol is separated from the paraffins by distillation, and the mononitrotoluol thus obtained freed from paraffins is nitrated to trinitrotoluol. This process is expensive, complicated and wasteful, as it involves acid-free washing of the mononitrotoluol before it is ready for distillation. Moreover, any higher nitro compounds present in the mononitrotoluol are lost in the shape of still-residue during such distillation. Besides, such distillation has been known to cause explosions. My process avoids such distillation and offers, therefore, considerable practical advantage.

In describing the process I shall, as an example, describe the several steps of the complete process for carrying the nitration of a typical toluol to trinitrotoluol, it being understood that while all the steps are not independently novel they have not heretofore been employed in connection with the novel steps of the process, for which reason they have not satisfactorily accomplished the results attained in the practice of my invention.

I take a toluol containing 13 per cent. of paraffin and showing the following distillation record:

| | |
|---|---|
| First drop | 109.3 |
| 2½% | 110.5 |
| 5% | 110.7 |
| 95% | 111.3 |
| 97½% | 111.4 |
| Dry | 111.4 |
| Specific gravity | .852 |

The toluol is then nitrated to mononitrotoluol in the following manner; 60.5 pounds of this toluol (containing therefore 52.5 pounds of pure toluol) are run into a nitrator and 133.8 pounds of mixed acid (one part of 74.7 per cent. nitric acid and 1.5 parts of 96 per cent. sulfuric acid) are then run into the nitrator, within four hours, with continued stirring, at a temperature gradually rising from 55° to 60° C. The stirring is then continued for two hours, the temperature being maintained at 60° C.

The mass is allowed to settle until the acid can be drawn off clear at the bottom. Only the mononitrotoluol plus paraffins are left in the nitrator.

The mononitrotoluol is then separated from the contained paraffin in the following way: 138 pounds of 96 per cent. sulfuric acid are run into the nitrator all at once and mixed with the mononitrotoluol by fifteen minutes' stirring. The mass is then allowed to settle for some hours, until the bottom layer, consisting of a solution of mononitrotoluol in sulfuric acid, runs off clear. This bottom layer is drawn off until the first drop of paraffin makes its appearance. The paraffins are then drawn off separately.

The next step is the nitration of the purified mononitrotoluol to trinitrotoluol. I take (say) one half of the above solution of sulfuric acid and mononitrotoluol and add, at a temperature of about 65° C., 69 parts of oleum (104 per cent.) and 109.5 parts of mixed acid containing 47.0% $HNO_3$, 50.0% $H_2SO_4$ and 3% water. The temperature is then allowed to rise at the rate of one degree

in three minutes until it has reached 90° C., at which point it is kept for one hour. It is then allowed to further rise at the rate of one degree in three minutes until a temperature of 110° is attained, at which it is kept for two hours. The temperature is then allowed to rise until 120° C. is reached, at which it is kept for four hours. The charge is then run into a crystallizer.

It is unnecessary to adhere rigidly to the precise directions respecting time, temperature and proportions of materials above set out, my object in precisely setting forth a preferred way of carrying out the process being to enable those skilled in the art to practice the process without the necessity of experiment.

The above described process, with such modification as those skilled in the art can supply, is also applicable to the manufacture of dinitrobenzol, the separation from paraffins taking place, by means of sulfuric acid, in the mononitrobenzol stage. The process is also applicable to the separation of paraffins from other nononitro derivatives of hydrocarbons of the benzol series.

Having now fully described my invention, what I claim and desire to protect by Letters Patent is:

1. The process of separating mononitrotoluol from contained paraffins which consists in mixing the same with sulfuric acid until the mononitrotoluol is dissolved therein and then separating the solution from the paraffins.

2. The process of separating mononitrotoluol from contained paraffins which consists in mixing the same with a substantially equal quantity by volume of sulfuric acid, and then separating the solution of mononitrotoluol and acid from the paraffins.

3. The process of manufacturing trinitrotoluol from toluol containing paraffins, which consists in nitrating the toluol to mononitrotoluol, then mixing the mononitrotoluol with sulfuric acid until the mononitrotoluol is dissolved therein and separating out the undissolved paraffins, and then nitrating the purified mononitrotoluol to trinitrotoluol.

4. The process of manufacturing trinitrotoluol from toluol containing paraffins, which consists in nitrating the toluol to mononitrotoluol, then adding to the mononitrotoluol a substantially equal quantity by volume of sulfuric acid to dissolve the mononitrotoluol, separating out the undissolved paraffins, and then nitrating the purified mononitrotoluol to trinitrotoluol.

5. The process which consists in nitrating a hydrocarbon of the benzol series containing paraffin to a mononitro derivative thereof, then mixing the said derivative with sulfuric acid until the said derivative is dissolved therein and separating out the undissolved paraffins, and then nitrating the purified derivative to a higher degree of nitration.

In testimony of which invention, I have hereunto set my hand, at New York, N. Y., on this 17" day of March, 1916.

BERNHARD JACQUES FLURSCHEIM.

Witnesses:
LAURA B. PENFIELD,
JOHN F. HEFFERMAN.