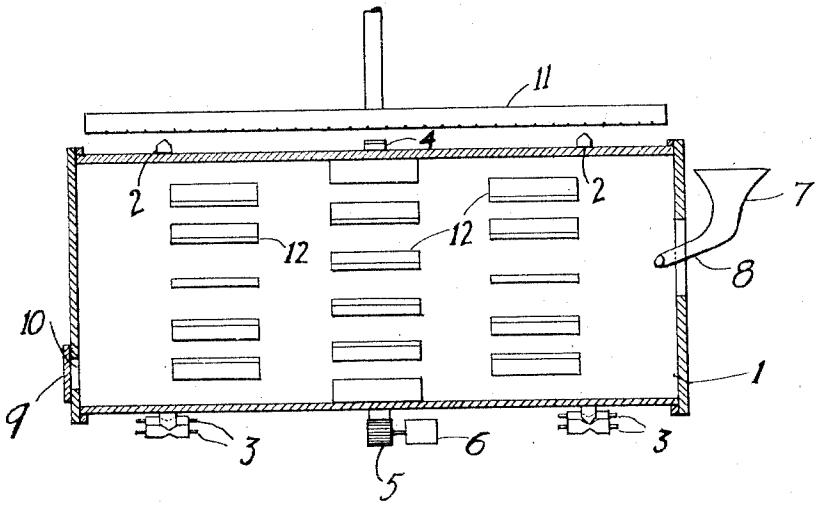
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METHOD OF REDUCING NITRO COMPOUNDS

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METHOD OF REDUCING NITRO COMPOUNDS

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This invention relates to the reduction of nitro-compounds. It relates more particularly to the reduction of nitro-compounds obtained from hydrocarbons and their derivatives for the purpose of obtaining amino compounds. The invention will be particularly described in connection with the production of naphthylamine from nitro-naphthalene and aniline from nitro-benzene although it is to be understood that it is not restricted to the production of these particular products.

It has been known a long time, for example, that nitro-naphthalene could be reduced to naphthylamine by charging nitro-naphthalene, hydrochloric acid, iron and water into a stationary, vertical or horizontal cast iron cylindrical vessel that was provided with a stirrer for agitating the mass, the temperature being maintained at a sufficiently high enough point to keep the nitro-naphthalene melted. Iron borings were fed in while agitating and effort was made to keep the temperature constant by keeping the iron vessel surrounded by a water jacket in which cool water was circulated. Nitro-naphthalene was in this way reduced to naphthylamine.

In carrying out a reduction process as above outlined many practical difficulties have been encountered. Mechanical troubles from the agitation of the materials arose as the presence of the iron borings or filings threw a heavy load upon the stirrer and made proper agitation difficult. It was very difficult to control the temperature as only a small portion of the walls were available for heat transfer since the materials were concentrated at the bottom of the vessel.

By the present invention the difficulties present with the prior practice are overcome, and reduction processes can be carried out in a very much more rapid and satisfactory manner.

The invention will be understood from the description in connection with the accompanying drawing which represents a longitudinal section through one type of the device that may be used for practicing the invention.

In the drawing, reference character 1 designates a vessel made of cast iron or other suitable materials whose axis is horizontal or at least not in a vertical plane. This vessel is similar in appearance to the well known rotary cement kilns and may be provided with rings 2 on its outer surface which rest upon rollers 3 which support the vessel and permit it to be revolved about its axis, or the vessel may be revolved in any other manner, to cause the contents to be tumbled. The vessel may, for example, be revolved by having a toothed ring 4 which surrounds and is attached to the vessel 1 and meshes with a pinion 5 driven from any convenient source of power 6 so that the vessel 1 may be revolved at the desired speed. A hopper 7 is provided with a feed pipe 8 which leads into the vessel 1 through which the materials may be introduced at one end and a removable cover plate 9 closes a hole 10 at the other end through which the products can be removed. The vessel 1 may be cooled in any convenient manner. For example, a perforated pipe 11 may be provided so that water may be sprayed upon the outside of the vessel for cooling purposes. Vanes 12 may be placed on the inside of the vessel 1 to aid in stirring or agitating and mixing the contents. If desired, a reflux condenser could be employed by means of which a considerable amount of heat could be removed. In this case the vessel 1 would be entirely closed and a pipe would lead through a stuffing box at the center of one head to the condenser.

As an illustration of the invention about 200 pounds of hydrochloric acid, 2,800 pounds of iron filings or borings or the like, and 500 gallons of water may be introduced into the vessel 1 and it is started to revolving. Alpha-nitro-naphthalene may then be introduced at the rate of about 10 pounds per minute until 2,500 pounds have been introduced and the reaction is permitted to continue until the reaction is substantially or sufficiently complete, when the vessel 1 is stopped and the contents removed.

As another illustration of the invention about 180 pounds of hydrochloric acid, 3,200 to 3,500 pounds of iron filings or borings or the like and about 125 gallons of water may

be introduced into the vessel 1 and it is started to revolving. Nitro-benzene may then be introduced at the rate of about 600 pounds per hour until 3,000 pounds have been introduced and the reaction is permitted to continue until test shows reduction to be complete. The process will also operate if the nitro compound, hydrochloric acid and water are introduced into the vessel 1 and the iron is slowly fed into the mixture; or the hydrochloric acid and water may be introduced into the vessel and then the nitro-compound and iron may be added.

The mixture of iron, nitro-compounds, hydrochloric acid, and water may be regulated so that there is an excess of reducing agent always present, or there may be an excess of the nitro-compound or material being reduced when this is found to be desirable, but it has been found that in most cases the reduction of nitro-compounds such as nitro-benzene, nitro-toluene, nitro-xylene, nitro-naphthalene and nitro-sulfonic acids of benzene and naphthalene as well as di-nitro-benzene and di-nitro-toluene, etc., can be accomplished most satisfactorily in the presence of an excess of the reducing agent. By first introducing the HCl, iron and water into the vessel 1 and afterwards gradually introducing the nitro-compound an excess of the reducing agent, iron, ferrous chloride and water are always present and the chemical reaction to produce the corresponding amino compound seems to be best promoted. The reduction proceeds more rapidly than when using the old process so that the time is shortened and the mechanical power required is considerably decreased below that required with a mechanical stirrer. The cooling is more readily regulated as the entire surface of the vessel is available for dissipation of the heat and the temperature can, therefore, be more readily kept within closer limits of temperature range than with the stationary vessel.

It is to be understood that this invention is not restricted to the use of iron, as other materials such as zinc dust, tin, or any of the other well-known reducing agents may be employed instead of iron.

A series of machines as above described may be so installed that the products from each one may be fed into the following one of the series thus providing a continuous process. In such an installation an excess of iron or reducing agent may be introduced into each of the machines and the nitro-compound, hydrochloric acid and water in proper proportions together with more iron if desired may be passed through the series. More iron may be added to the individual machines from time to time as needed and the liquid nitro bodies flow from one machine to the next and so on through the series finally issuing from the last one completely reduced and carrying in suspension a large portion of the iron oxide formed during the reduction.

I claim:

1. The process which comprises introducing iron, an acid and water into a vessel revoluble about a non-vertical axis and introducing into said vessel, while it is revolving, an aromatic nitro-compound at such a rate that a reducing agent is always present.

2. The process which comprises introducing iron, hydrochloric acid and water into a vessel revoluble about a non-vertical axis, cooling said vessel and introducing into said vessel, while it is revolving, nitronaphthalene at such a rate that a reducing agent is always present.

3. A process for the reduction of nitro bodies by adding the same to a reducing agent in a vessel revoluble about a non-vertical axis which comprises gradually adding said nitro bodies while rotation said vessel, applying a cooling fluid to the exterior of said vessel and dissipating the reaction heat as rapidly as formed by thermal contact of the mixture with the vessel walls.

4. The method of effecting the reduction of aromatic nitro-compounds which comprises introducing one or more reagents for effecting the reduction of a nitro-compound into a vessel, passing a cooling fluid over the exterior of said vessel, distributing the reagents over substantially the entire inner surface of the vessel by rotation of the vessel and introducing the nitro-compound to be reduced into the vessel while the vessel is in motion.

5. The method of effecting the reduction of aromatic nitro-compounds which comprises introducing one or more reagents for effecting the reduction of a nitro-compound into a vessel revoluble about a non vertical axis, distributing the reagents over substantially the entire inner surface of the vessel by rotation of the vessel, introducing the nitro-compound to be reduced into the vessel while the vessel is in motion, applying a cooling fluid to the exterior of said vessel and controlling the temperature of the reaction by heat exchanged through the walls of the vessel.

6. The method of effecting the reduction of aromatic nitro-compounds which comprises forming a pool of a portion of the materials which are to take part in the reaction, moving a heat exchanging surface in contact with the materials upwardly from the surface of the materials whereby the moving surface carries a portion of the materials therewith, bringing a cooling fluid into heat-exchange relation with said surface, and adding the remaining materials which are to take part in the reaction to the materials in the pool while the heat exchanging surface is in motion.

7. The method of effecting the reduction of aromatic nitro-compounds which comprises the steps of introducing the reaction materials into a vessel, maintaining an excess of the reagents for effecting the reduction of the nitro-compounds in the vessel by adding the nitro-compound gradually to the reaction materials as the reaction proceeds and controlling the temperature of the reaction materials during operation to obtain the maximum yield of the reduction compound by applying a cooling fluid to the exterior of said vessel and effecting heat exchange through the walls of the vessel over substantially the entire surface thereof.

8. The method of effecting the reduction of aromatic nitro-compounds which comprises the steps of introducing the reaction materials into a vessel revoluble about a non-vertical axis, maintaining an excess of the reagents for effecting the reduction of the nitro-compound in the vessel by adding the nitro-compound gradually to the reaction materials as the reaction proceeds, controlling the temperature of the reaction materials during operation to obtain the maximum yield of the reduction compound by cooling the exterior of the vessel, effecting heat exchange through the walls of the vessel by revolving the vessel about its axis and distributing the reaction materials over the interior walls of the vessel throughout substantially the entire surface thereof.

9. The method of reducing nitronaphthalene to produce naphthylamine which comprises the steps of introducing the reaction materials into a vessel revoluble about a non-vertical axis, maintaining an excess of the reagents for effecting the reduction of the nitronaphthalene in the vessel by adding the nitronaphthalene gradually to the reaction materials as the reaction proceeds, controlling the temperature of the reaction materials to obtain the maximum yield of naphthylamine by spraying water onto the exterior of the vessel in which the reaction takes place to cool the walls thereof while effecting heat exchange through the walls of the vessel by revolving the vessel about its axis and distributing the reaction materials over the inner walls of the vessel throughout substantially the entire surface thereof.

In testimony whereof I affix my signature.

STUART P. MILLER.