It therefore seemed desirable to turn to the mononitrotoluene as a medium for purification. Toluene is associated with paraffins and olefins of boiling points in the neighborhood of 110° C. By washing with sulphuric acid, the olefins are extracted. By nitration, toluene may be converted to mononitrotoluene, boiling at 218° to 238° C., whereas paraffins remain unchanged or are in part polymerized to resinous bodies. In the resultant mixture the desired mononitrotoluene is separable from the others by a process of fractional distillation. This separation may be readily accomplished, although distillation in a vacuum or with steam gives the best results. The following scheme of procedure is that which has been found most satisfactory and most economical.

Wash the mixture of toluene, paraffin, olefin, etc., with sulphuric acid of a specific gravity of 1.84 to take out unsaturated hydrocarbons or olefins. A mixture of aromatics and paraffins remains that is saturated with sulphuric acid. The latter does not need removal, as it is one of the reagents involved in the next step. The acid-toluene-paraffin mixture is then treated with a reagent consisting of mixed nitric acid and sulphuric acid strong enough to attack toluene. The concentration of the acid varies with the proportion of paraffins present. The impure mixture obviously requires less acid than would pure toluene. The acid is withdrawn from the nitrated mixture and the latter, after having been washed with water, is distilled in a vacuum or with steam, air distillation being undesirable on account of its producing a certain degree of decomposition.

RESULTS AND BEARING OF NITRATION EXPERIMENTS.

Actual experiments along the lines just indicated have been conducted in the Bureau of Mines laboratory. By the simple process of deolefinization with sulphuric acid, nitration of the unwashed product, and a single vacuum distillation samples of mononitrotoluene have been prepared that on analysis showed nitrogen contents within 0.5 per cent of the theoretical. Yields in laboratory experiments are necessarily lower than can be obtained under commercial conditions, but even here results have been obtained that show a recovery of pure product of 75 to 82 per cent of the total theoretically possible, comparing favorably with the recovery of toluene from coal tar.

The simplicity of this procedure indicates an advantage of petroleum over coal tar as a source of toluene. The product from coal tar may, it is true, be obtained in a pure state, but the processes are complicated and expensive owing to the necessity of removing oxygen and sulphur bodies derived from coal. The toluene derived from tar must be given extensive treatment both by distillation and by washing with chemicals before it can be utilized in nitration processes.

Petroleum-derived toluene is not so easily obtainable in a pure state, but its impurities are not of such nature as to cause trouble when the process of nitration is carried out. In short, there are two simple processes for deriving toluene from petroleum and one difficult process for deriving it from coal tar.

If the operation of nitration is conducted on a large scale, the purity of the mononitrotoluene obtained is highly satisfactory, and makes what has been considered a serious objection a real advantage, in that it is easy to use any petroleum-derived toluene without regard to its state of purity. Instead of attempting to obtain pure toluene at the outset the effort to reach a state of chemical purity is made at the mononitrotoluene stage.

Petroleum-derived toluene is partly purified by distillation, and then mononitrotoluene is prepared, which is completely purified by a distillation with steam or in a vacuum.

The actual preparation of trinitrotoluene from petroleum-derived mononitrotoluene has been accomplished by a modification of the two-stage process in use by one of the large explosive companies of this country. The products obtained, after having been washed with water, satisfied the present customary specification of a melting point above 75° C. The yields have approximated 75 per cent of the yields theoretically possible. Here, again, the factor of yield has not been studied with the care bestowed on quality, as laboratory figures can not at best compare with those obtained in commercial operations.

NITRATION OF BENZENE BY METHOD APPLIED TO TOLUENE.

The utilization of benzene obtained from cracked petroleum has not yet been studied with the care bestowed on the utilization of toluene. Experiments for the preparation of picric acid are now in progress. Nitrobenzene has been obtained by a method identical with that involved in the preparation of nitrotoluene. From such nitrobenzene an 85 per cent yield of aniline oil has been obtained, the latter being one of the more important raw materials in the dyestuff industry.

The general conclusion is that the difficulty of utilizing aromatic hydrocarbons derived from petroleum is slight, requiring only necessary deviations from the conventional methods applied to the carefully purified products obtained from coal.

EXPERIMENTS TO DETERMINE COURSE OF REACTION AMONG AROMATIC HYDROCARBONS.

The series of experiments dealing with general transformations was accompanied by studies that went more into detail regarding the specific products obtained by the cracking reaction. The following considerations have proven of the greatest importance in the present study, and accordingly are given separate and detailed discussion.