

# UNITED STATES PATENT OFFICE.

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## PROCESS OF OXIDIZING METHYL GROUPS IN AROMATIC HYDROCARBONS.

SPECIFICATION forming part of Letters Patent No. 780,404, dated January 17, 1905.

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*To all whom it may concern:*

Be it known that we, MAX BAZLEN, a subject of the King of Württemberg, and HANS LABHARDT, a citizen of the Swiss Republic, both residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria, Empire of Germany, have invented new and useful Improvements in Processes of Oxidizing Methyl Groups of Aromatic Hydrocarbons, of which the following is a specification.

We have discovered that manganese persulfate or, as it might be termed, the "sulfate of manganese peroxid" can be used for the oxidation of the methyl groups in aromatic hydrocarbons and derivatives thereof. The said manganese persulfate can, for instance, be obtained if manganous sulfate be treated in moderately-concentrated sulfuric-acid solution with electrolytic oxygen until the red solution of manganic sulfate, which is at first obtained or, as the case may be, the precipitate thereof is converted into a brown solution.

We have discovered that the acid solution of manganese persulfate has the property of oxidizing the side chains—that is, the methyl or substituted methyl group—in aromatic hydrocarbons and their derivatives, so as to convert them into the aldehyde group. This new reagent acts in a different way from and is far better suited for use for this purpose than is a mixture of manganese peroxid and sulfuric acid. The reaction proceeds energetically under conditions under which manganese peroxid and sulfuric acid have practically no action. The new process is of very general application. Toluene gives a good yield of benzaldehyde, and the homologues of toluene and its substitution products, as also benzyl alcohol and its esters, behave similarly. The process is of particular value for the production of orthonitrobenzaldehyde from orthonitrotoluene, for the yield of this body that can be obtained by the new process is twice as great as that hitherto obtained by the best-known process from orthonitrobenzaldehyde, manganese peroxid, and concentrated sulfuric acid.

If the oxidation be conducted more ener-

getically—for instance, by the use of a higher temperature and a sufficient quantity of oxidizing agent—the corresponding carboxylic acids can be obtained in some cases in admixture with aldehydes.

The new process has the further advantage that the resulting sulfuric-acid solution of manganous sulfate can readily be converted by electrolytic oxidation into manganese persulfate which can again be used, whereas it has not generally paid to regenerate the manganese peroxid hitherto used when oxidizing with this reagent and sulfuric acid.

The following examples will serve to further illustrate our invention; but it is not confined to these examples. The parts are by weight.

Example 1: Prepare a solution of manganese persulfate, for instance, by electrolytically oxidizing a solution of six hundred parts of manganous sulfate ( $\text{MnSO}_4 + 4\text{H}_2\text{O}$ ) in twenty-nine hundred parts of sulfuric acid, (containing about fifty-five per cent. of  $\text{H}_2\text{SO}_4$ .) This can be effected by using a lead anode and a cell furnished with a diaphragm, keeping the temperature at from about  $50^\circ$  to  $60^\circ$  centigrade and using a current having a density of about fifteen to sixteen amperes per square decimeter at the anode and a tension of from four to four and a half volts. In this way a solution should be obtained containing from about twelve to fifteen per cent. of manganese persulfate. Run this solution slowly during a period of from four to five hours into five hundred parts of orthonitrotoluene at a temperature of from  $50^\circ$  to  $60^\circ$  centigrade. Stir continuously during the addition and subsequently. When the solution is decolorized, distil off the orthonitrobenzaldehyde formed and the excess of orthonitrotoluene in a current of steam. Conduct this operation preferably in such a way that the sulfuric acid maintains its concentration. Isolate the aldehyde from the distillate in the well-known manner. The sulfuric-acid solution of manganous sulfate remaining can at once be oxidized electrolytically and used again for a new operation.

Example 2: Prepare a solution of manga-



nese persulfate as described in Example 1 and add to this three hundred parts of toluene. The addition is effected gradually during a period of about four hours while thoroughly stirring and maintaining the temperature at from about 40° to 50° centigrade. Distil off the benzaldehyde and toluene in a current of steam and separate the benzaldehyde in the usual way. Benzoic acid is not produced under these conditions. The only by-product is very small quantity of resinous matter.

To produce benzoic acid, proceed as follows: Run thirty parts of benzaldehyde, while stirring thoroughly, into five hundred parts of a solution of manganese persulfate containing, say, nine-tenths per cent. of active oxygen. The reaction proceeds very slowly in the cold, and even at the temperature of the water-bath several hours are necessary. The yield is practically quantitative. Of course, if desired, the oxidation of the toluene to benzoic acid can be effected in one operation without the intermediate isolation of the aldehyde.

Example 3: Prepare an emulsion of about one hundred parts of benzyl alcohol and seven hundred and fifty parts of dilute sulfuric acid (containing fifty-five per cent. of  $H_2SO_4$ ) by stirring the substances together with the aid of an effective stirrer. Add to this emulsion drop by drop five hundred and seventy parts of manganese persulfate, (containing about seventy-nine hundredths per cent. of active oxygen.) The oxidation proceeds rapidly at a temperature of from 40° to 50° centigrade. When the solution is decolorized, drive off the benzaldehyde formed with steam. To separate the benzyl alcohol that passes

over with it, the benzaldehyde can be converted into its bisulfite compound. The benzyl alcohol that is not oxidized can be recovered almost quantitatively. Only traces of benzoic acid are formed under the conditions described.

Example 4: Mix together thirty parts of benzyl chlorid and seven hundred and fifty parts of sulfuric acid, (containing fifty-five per cent. of  $H_2SO_4$ .) Add to the emulsion gradually about one thousand parts of manganese-persulfate solution, (containing about seventy-nine hundredths per cent. of active oxygen.) Heat the mixture on the boiling-water bath. The oxidation occupies from three to four hours. A mixture is obtained of unchanged initial material, with benzoic acid as the principal product with a little benzaldehyde. A small quantity of benzyl alcohol is converted into resinous products.

We claim—

1. The process for the oxidation of the side chains in aromatic derivatives by treating them with an acid solution of manganese persulfate.

2. The process for the oxidation of the methyl group in orthonitrotoluene to the CHO group by treating it with an acid solution of manganese persulfate.

In testimony whereof we have hereunto set our hands in the presence of two subscribing witnesses.

MAX BAZLEN.  
HANS LABHARDT.

Witnesses:

JOHN L. HEINKE,  
JACOB ADRIAN.