

UNITED STATES PATENT OFFICE.

MAX BAZLEN, OF LUDWIGSHAFEN, GERMANY, ASSIGNOR TO BADISCHE ANILIN & SODA FABRIK, OF LUDWIGSHAFEN, GERMANY, A CORPORATION OF BADEN, GERMANY.

PROCESS OF MAKING AROMATIC ALDEHYDE AND ACID.

SPECIFICATION forming part of Letters Patent No. 698,355, dated April 22, 1902.

Application filed March 16, 1901. Serial No. 51,497. (No specimens.)

To all whom it may concern:

Be it known that I, MAX BAZLEN, doctor of philosophy and chemist, a subject of the King of Württemberg, residing at Ludwigs-
5 hafen-on-the-Rhine, in the Kingdom of Bavaria and Empire of Germany, have invented new and useful Improvements in the Manufacture of Aromatic Aldehydes and Acids, of which the following is a specification.

10 It is known that aldehydes can be obtained from aromatic hydrocarbons containing a methyl group and certain of their derivatives, such as are mentioned in the specifications of Patents No. 613,460, November 1, 1898;
15 No. 650,332, May 22, 1900; No. 661,872, November 13, 1900; No. 677,239, June 25, 1901—for example, toluene, xylene, nitro-toluene, and the like—by oxidizing the said bodies with manganese peroxid, with or without the
20 addition of sulfuric acid.

I have discovered that the oxidation of the substances to which I have above referred (to which I hereinafter apply the generic term
25 "toluene substance" as including all of them) to aldehydes can be effected by means of certain oxids which have never been employed before for this purpose and which have the property of decomposing sodium-hypochlorite solution, (thereby generating oxygen)—
30 namely, the so-called "peroxid" of nickel or cobalt—the oxidation taking place in the presence or absence of sulfuric acid. In addition to aldehyde a certain amount of the corresponding carboxylic acid is, as a rule,
35 formed during the reaction. Hereinafter I apply the term "peroxid" to that oxid which can be obtained from the hydrochloric salt of the metal in question, caustic soda, and chlorin. The oxidation takes place in most
40 cases at or below a temperature of one hundred (100°) degrees centigrade; but the temperature can of course be varied without departing from my invention. For example, the body to be oxidized is heated with dry
45 nickel peroxid (which can be prepared from nickel salts in the well-known manner by means of alkali and chlorin or bromin or sodium hypochlorite) in the boiling-water bath for from five (5) to six (6) hours, the oxida-

tion product formed and unattacked initial 50 material are separated from the nickel oxid by filtration or distillation in steam, and the aldehyde is isolated from the filtrate or distillate in the well-known manner by means of sodium bisulfite. The oxidation can also be 55 carried out by directly passing steam into the mixture of nickel oxid and the body to be oxidized, thus distilling off the aldehyde as it is formed, together with unchanged initial material. The organic acid which is formed in 60 addition to the aldehyde and which corresponds to the hydrocarbon used as initial material—for example, benzoic acid being obtained from toluene, ortho-nitro-benzoic acid from ortho-nitro-toluene, and so on—can be 65 isolated by filtering the liquid remaining in the distilling vessel, concentrating the filtrate, and acidifying the same with hydrochloric acid. The amount of organic acid formed can be diminished by adding a nickel 70 or cobalt salt—for example, nickel chlorid (NiCl₂)—or a small quantity of an acid, such as sulfuric acid, to the reaction mixture. In the course of the reaction the nickel peroxid is reduced in part or entirely to a lower oxid, 75 which can be reconverted by means of a suitable oxidizing agent—for example, sodium-hypochlorite solution—into the original oxid and at once used again, or the lower oxid formed can be retransformed into the origi- 80 nal peroxid during the course of the reaction by slowly adding a suitable oxidizing agent, such as sodium hypochlorite, to the reaction mixture.

The following examples will serve to fur- 85 ther illustrate the nature of my invention and the best manner I know of carrying it into practical effect; but I do not confine myself to the details therein given. The parts are by weight. 90

Example 1: Heat together three hundred (300) parts of toluene with one hundred and fifty (150) parts of nickel peroxid at a temperature of one hundred (100°) degrees centigrade for from five (5) to six (6) hours. Fil- 95 ter the liquid from the nickel body and separate the benzaldehyde formed from unaltered toluene by shaking the mixture with

aqueous sodium-bisulfite solution and isolate the aldehyde in the well-known manner.

Example 2: Mix together three hundred (300) parts of ortho-nitro-toluene, fifty (50) parts of nickel peroxid, and five (5) parts of nickel chlorid, (NiCl_2 .) Pass steam into the mixture while slowly running in ten (10) parts, by volume, of sodium-hypochlorite solution, (containing ten per cent. of active chlorine.) When nothing more comes over with the steam, isolate from the distillate the ortho-nitro-benzaldehyde formed by means of sodium bisulfite in the well-known manner. To obtain the ortho-nitro-benzoic acid formed, filter the contents of the distilling vessel, concentrate the filtrate, and acidify it with hydrochloric acid. The ortho-nitro-benzoic acid separates out.

The nickel chlorid in the above example can be replaced, for instance, by four (4) parts of sulfuric acid (containing one hundred per cent. of H_2SO_4) or by a suitable quantity of hydrochloric or other acid acting similarly. In every case cobalt peroxid or a cobalt salt can be employed instead of nickel peroxid or a nickel salt, respectively.

In place of the sodium hypochlorite employed in the preceding examples there may be employed calcium hypochlorite, potassium hypochlorite or sodium, potassium or calcium

hypobromites, to all of which I hereinafter apply the generic term "oxidizing agent."

Now what I claim is—

1. The process of making aromatic aldehyde and acid which consists in treating a hereinbefore-defined toluene substance with the peroxid of a metal of the nickel group, a salt of a metal of the nickel group and a suitable oxidizing agent.

2. The process of making aromatic aldehyde and acid which consists in treating a hereinbefore-defined toluene substance with the peroxid of a metal of the nickel group and a salt of a metal of the nickel group.

3. The process of making aromatic aldehyde and acid which consists in treating a hereinbefore-defined toluene substance with the peroxid of a metal of the nickel group.

4. The process of making ortho-nitro-benzaldehyde and ortho-nitro-benzoic acid which consists in treating ortho-nitro-toluene with nickel peroxid, nickel chlorid and sodium hypochlorite.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

MAX BAZLEN.

Witnesses:

JOHN L. HEMKE,
PAUL JULIUS.