

UNITED STATES PATENT OFFICE.

EUGEN SAPPER AND FRIEDRICH REUBOLD, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, ASSIGNORS TO BADISCHE ANILIN UND SODA FABRIK, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, A CORPORATION OF BADEN.

SULFO-ACID ESTER AND PROCESS OF MAKING SAME.

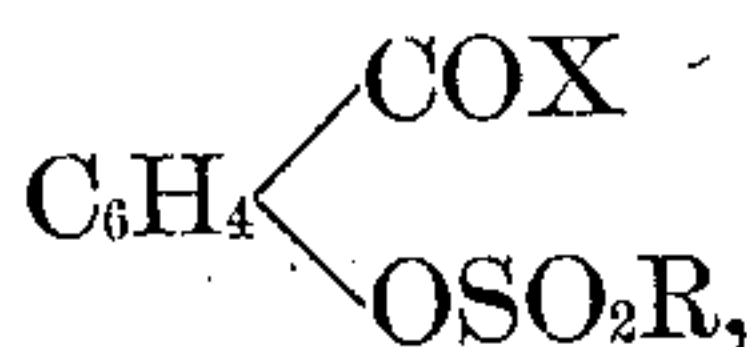
SPECIFICATION forming part of Letters Patent No. 765,597, dated July 19, 1904.

Application filed August 27, 1903. Serial No. 171,018. (Specimens.)

To all whom it may concern:

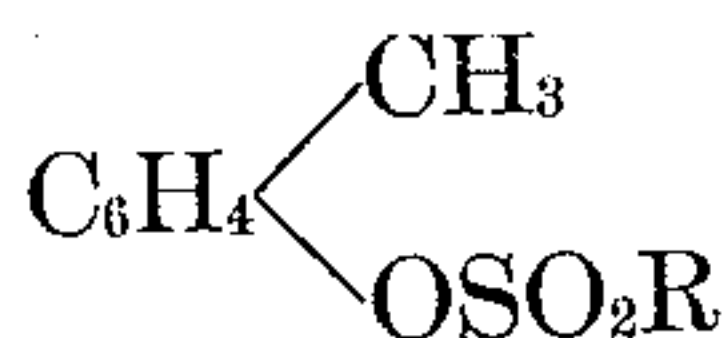
Be it known that we, EUGEN SAPPER, doctor of science, and FRIEDRICH REUBOLD, doctor of philosophy and chemist, subjects of the King of Bavaria, residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria, Empire of Germany, have invented new and useful Improvements in Sulfo-Acid Esters and Process of Making the Same, of which the following is a specification.

We have invented a new process for preparing bodies of the general formula



where X denotes hydrogen or hydroxyl and R an aryl radical.

The process consists in treating under suitable conditions the esters of cresols and aryl sulfo-acids of the general formula



with manganese dioxid and sulfuric acid, whereby sulfo-acid esters of hydroxybenzaldehyde or hydroxybenzoic acid, or both, result. These compounds can be converted by saponification into the corresponding hydroxybenzaldehydes or hydroxybenzoic acids and an aryl sulfo-acid. They are practically insoluble or difficultly soluble in water; but they are soluble in alcohol and ether. The saponification of the said compounds can be effected in any suitable known manner—for instance, by treatment with concentrated sulfuric acid in the cold or on gently warming or by boiling with caustic-soda lye.

The aforementioned esters of cresols and aromatic sulfo-acids can be obtained by the action of an aryl sulfochlorid—such as benzene-sulfochlorid, para-toluene-sulfochlorid, or ortho-toluene-sulfochlorid—on an aqueous solution of a cresol in warm dilute caustic-soda lye according to the method of Schotten and Baumann, and they can generally be obtained in crystalline form from ethyl alco-

hol. Some of the sulfo-acid esters of hydroxybenzaldehydes which can be obtained by the new process are known; but it also yields a large number of new products, and in particular those obtained when using toluene-sulfochlorid are new and possess a high value.

The following example will serve to further illustrate the nature of our invention; but it is not confined to this example. The parts are by weight:

Example: Heat together at the temperature of the boiling-water bath, while stirring well, five hundred parts (500) of toluene sulfo-acid ester of orthocresol with eight hundred (800) parts of sulfuric acid containing from seventy to eighty (70 to 80) per cent. of H_2SO_4 and three hundred (300) parts of finely-ground manganese dioxid. Owing to the heat of the reaction, the temperature of the reaction mass generally rises at first above one hundred degrees centigrade (100°C.) After stirring for from four to five (4 to 5) hours at the temperature of the boiling-water bath dilute the contents of the vessel with about nine hundred (900) parts of water and allow the whole to stand in a warm place. The product of the reaction separates out as an oil. Separate it from the aqueous layer and the manganese mud in any convenient manner and well mix it with a cold dilute solution of caustic soda. Filter and acidify the filtrate. The toluene sulfo-acid ester of salicylic acid is precipitated. Stir up the reaction product remaining undissolved with two hundred and fifty (250) parts of sodium-bisulfite solution containing about forty (40) per cent. of NaHSO_3 , thereby converting the aldehyde into its bisulfite compound. Dissolve it by the addition of water and filter it or separate it in any convenient manner from unaltered cresol ester. To the filtered bisulfite solution add acid or alkali, whereby the toluene sulfo-acid ester of salicylic aldehyde is precipitated, generally as an oily mass, which, however, soon solidifies to crystals. It can be purified by recrystallization from alcohol. The unaltered cresol ester can be employed for another operation. In a similar manner the oxidation of other cresol

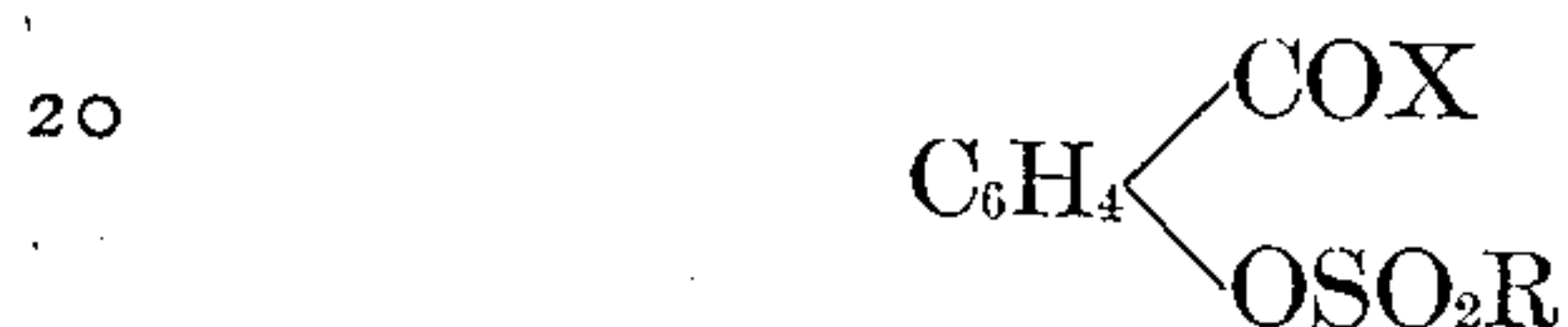
esters and mixtures of them can be performed. The aldehydes so obtained are white crystalline bodies which melt below a temperature of one hundred degrees centigrade, (100° C.)

5 They are difficultly soluble in water and easily soluble in ether and in hot alcohol.

The concentration and quantity of sulfuric acid, as also the quantity of the manganese dioxid, and the temperature of the reaction
10 can be varied within certain limits. A greater dilution of the acid, for example, can be compensated for by the employment of a larger quantity of it or by raising the temperature. The best conditions for each single case must
15 be determined by experiment.

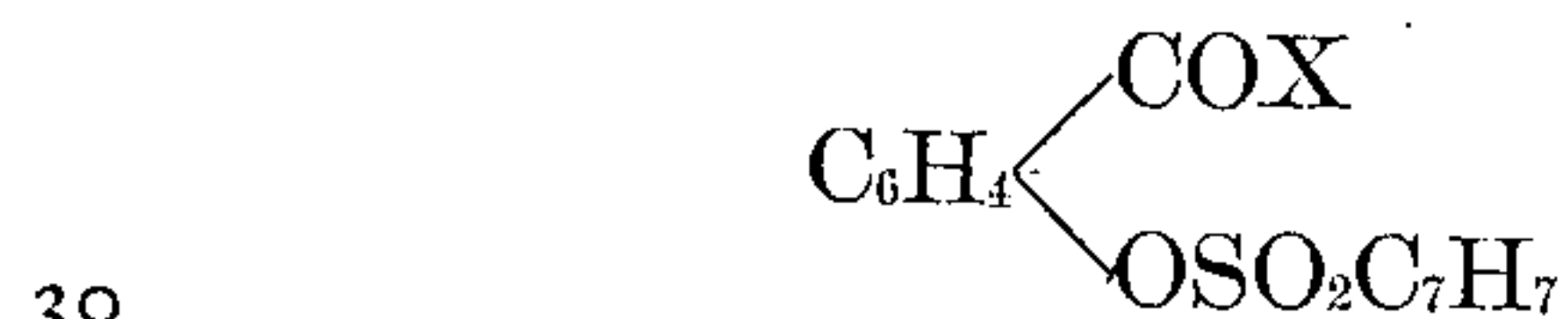
We claim—

1. The process of manufacturing bodies of the hereinbefore-explained general formula



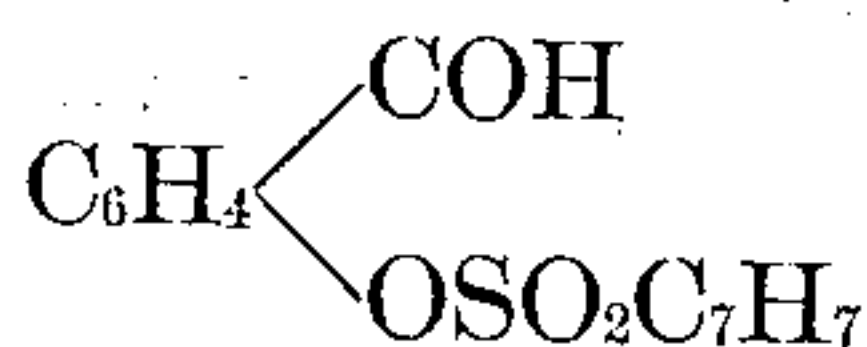
by treating the cresol esters of aryl sulfo-acids with manganese dioxid and sulfuric acid.

25 2. The process of manufacturing bodies of the hereinbefore-explained general formula



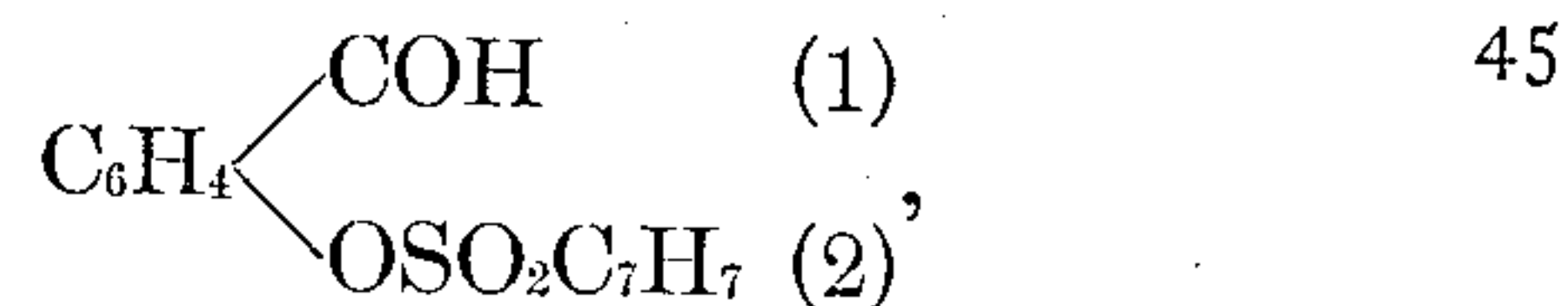
by treating the cresol esters of para-toluene sulfo-acid with manganese dioxid and sulfuric acid.

35 3. The process of manufacturing bodies of the formula



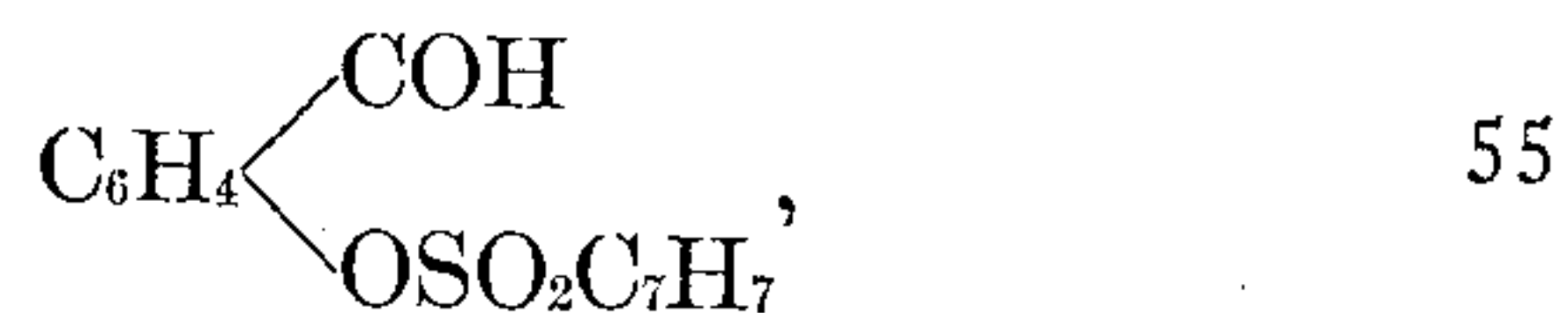
40 by treating the cresol esters of para-toluene sulfo-acid with manganese dioxid and sulfuric acid:

4. The process of manufacturing a body of the formula



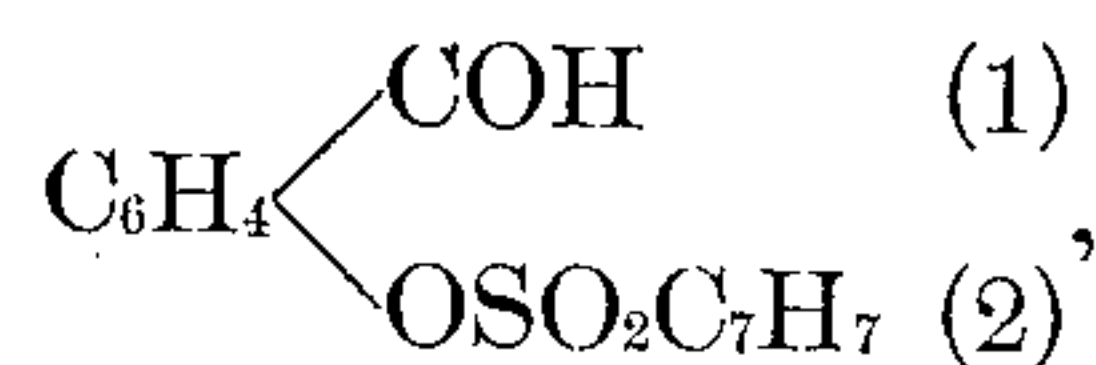
by treating the orthocresol ester of para-toluene sulfo-acid with manganese dioxid and
50 sulfuric acid.

5. As new articles of manufacture, the bodies of the formula



which are white crystalline bodies, which are difficultly soluble in water, but are easily soluble in ether and in hot alcohol, which melt
60 below a temperature of 100° centigrade and which on saponification yield para-toluene sulfo-acid and hydroxybenzaldehyde.

6. As a new article of manufacture, the body of the formula
65



which is a white crystalline body, which is
70 difficultly soluble in water, but is easily soluble in ether and in hot alcohol, which melts below a temperature of 100° centigrade, and which on saponification yields para-toluene sulfo-acid and ortho-hydroxybenzaldehyde. 75

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

EUGEN SAPPER.
FRIEDRICH REUBOLD.

Witnesses:

JACOB ADRIAN,
H. W. HARRIS.