

UNITED STATES PATENT OFFICE.

DANIEL TYRER, OF STOCKTON, ENGLAND.

SULFONATION OF HYDROCARBONS.

1,210,725.

Specification of Letters Patent. Patented Jan. 2, 1917.

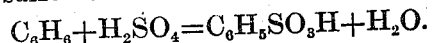
No Drawing.

Application filed May 22, 1916. Serial No. 99,252.

To all whom it may concern:

Be it known that I, DANIEL TYRER, a subject of the King of Great Britain, residing in Stockton-on-Tees, England, have invented a certain new and useful Sulfonation of Hydrocarbons, of which the following is a specification.

In sulfonating hydrocarbons the usual practice is to heat the hydrocarbon with strong sulfuric acid or fuming sulfuric acid, whereby water is eliminated. For example, in sulfonating benzene to monosulfonic acid it has hitherto been customary to heat together liquid benzene and the strongest sulfuric acid in a reflux apparatus. The acid slowly dissolves the benzene, forming the sulfonic acid and water—



In this operation, whether conducted with benzene or any other hydrocarbon, the temperature cannot rise much above the boiling point of the hydrocarbon and if this boiling point is not much above that of water the water eliminated remains to a great extent in the mass, with the result that the reaction ceases when there is still a large proportion of sulfuric acid not converted into sulfonic acid.

By my invention I sulfonate hydrocarbons which boil at temperatures below 200° C. by heating the hydrocarbon with sulfuric acid and removing from the mass, while the reaction is proceeding, the water eliminated by the reaction. The best procedure is to pass the vapor of the hydrocarbon through sulfuric acid heated to a temperature at which the water eliminated passes away with the excess of hydrocarbon vapor. This temperature depends on the boiling point of the hydrocarbon and the degree of sulfonation required, but should exceed 100° C.

As an example of the invention I will describe the sulfonation of benzene to the monosulfonic acid.

Into a cast iron still provided with a jacket for heating it by superheated steam is charged a quantity, say 20 kilos, of sulfuric acid which may be weaker, for instance of 90 per cent. strength, than can be used at the start when operating by the previously known method; herein resides a further advantage of the invention. The temperature of the acid having been raised to about 100° C., benzene vapor is passed from

a boiler containing benzene through a pipe extending below a perforated cast iron plate situated near the bottom of the still; this plate acts as a distributor of the vapor through the acid. The heating of the still is continued in such manner that the temperature of the acid, as indicated by a thermometer in the still, rises by about 1° C. per minute until it is about 185° C. at which it is maintained for about half-an-hour. Throughout the operation benzene vapor and water vapor are condensed in the condenser attached to the still. The liquids separate into two layers in the receiver and the benzene is drawn off and returned to the boiler. At the end of the said half hour the contents of the still consist mainly of benzene monosulfonic acid, that is to say about 80 per cent. of the amount theoretically obtainable with the sulfuric acid used.

If a stronger acid is used or the temperature is high, say 160° C., from the start, more or less benzenedisulfonic acids are produced, but by working under the conditions named the amount of monosulfonic acid formed while the temperature is rising from 100° C. dilutes the acid below the strength at which sulfonation can proceed beyond the mono-stage.

When it is the object to make benzenedisulfonic acids, it is better to proceed first to the mono-stage as described above and then to add more strong sulfuric acid and continue the heating.

Other hydrocarbons may be similarly sulfonated.

Having thus described the nature of the said invention and the best means I know of carrying the same into practical effect, I claim:

1. A process of sulfonating hydrocarbons which boil at temperatures below 200° C., which process consists in heating the hydrocarbon with sulfuric acid and removing from the mass, while the reaction is proceeding, the water eliminated by the reaction.

2. A process of sulfonating hydrocarbons which boil at temperatures below 200° C., which process consists in passing the vapor of the hydrocarbon through sulfuric acid heated to a temperature exceeding 100° C.

3. A process of sulfonating benzene, which process consists in passing vapor of benzene through sulfuric acid heated to a temperature exceeding 100° C.

4. A process of sulfonating benzene to monosulfonic acid, which process consists in passing vapor of benzene through sulfuric acid heated to a temperature exceeding 100° C.
5. A process of sulfonating benzene to monosulfonic acid which process consists in heating strong sulfuric acid to about 100° C. and passing benzene vapor through the heated acid while the temperature of the latter is gradually raised to about 185° C., and maintained thereat until benzene vapor ceases to be absorbed.
6. A process of sulfonating benzene to monosulfonic acid, which process consists in heating strong sulfuric acid to about 100° C., and passing benzene vapor through the heated acid while the temperature of the latter is gradually raised to about 185° C. and maintained thereat for half-an-hour.
7. A process of sulfonating benzene to monosulfonic acid, which process consists in heating strong sulfuric acid to about 100° C., and passing benzene vapor through the heated acid while the temperature of the latter is gradually raised to about 185° C. at the rate of about 1° C. per minute, and maintained thereat for half-an-hour.
8. A process of sulfonating benzene to monosulfonic acid, which process consists in passing vapor of benzene through sulfuric acid of 90 per cent. strength heated to a temperature exceeding 100° C.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

DANIEL TYRER.

Witnesses:

B. PEAT,
ARTHUR G. BAKER.