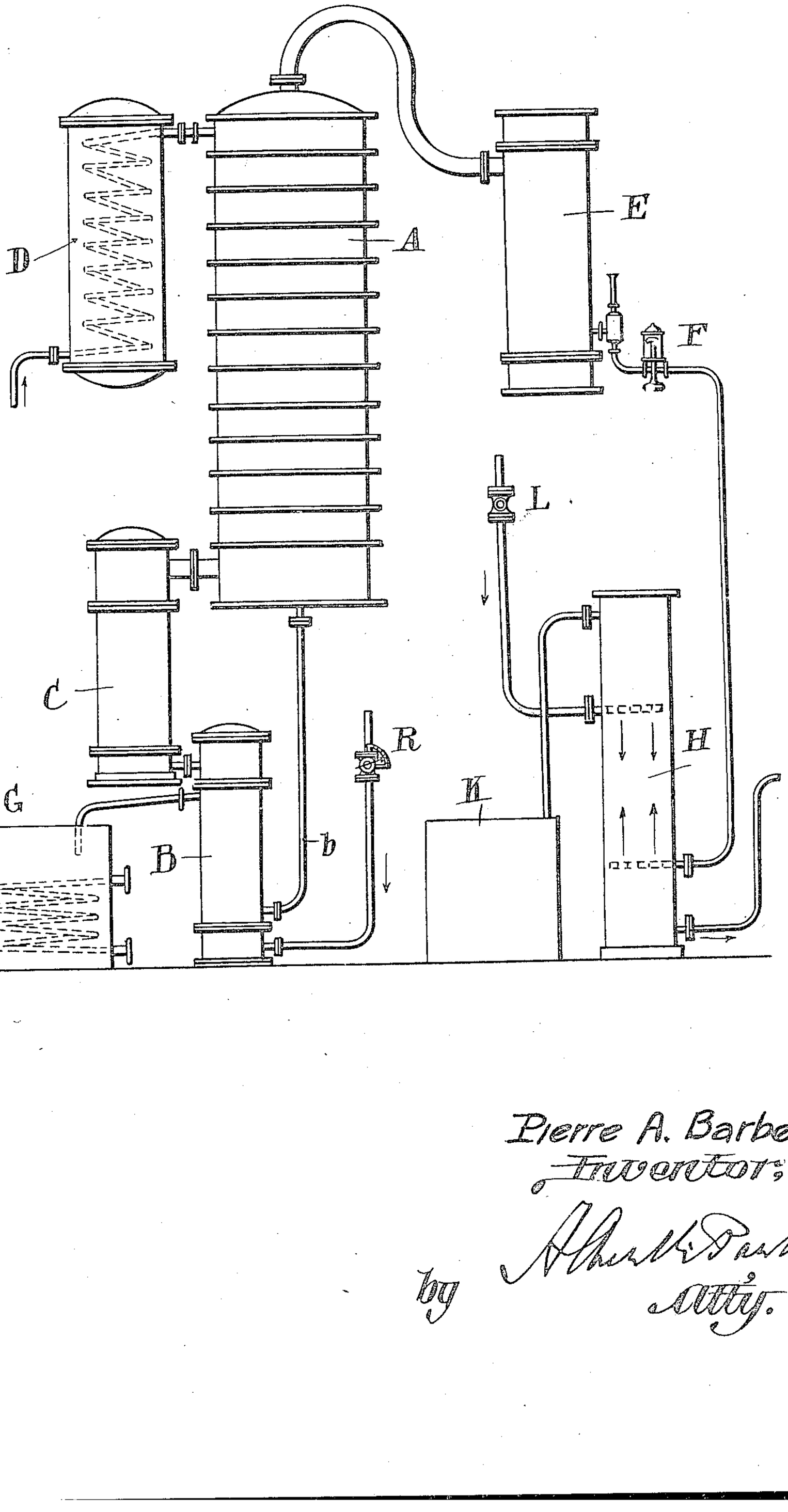
June 19, 1923. 1,459,081

P. A. BARBET

PROCESS OF CONTINUOUS SULPHONATION OF BENZENE, APPLICABLE TO IMPURE BENZENES

Filed April 23, 1917



Pierre A. Barbet.
Inventor;
by Albert G. Davis
Atty.

Patented June 19, 1923. 1,459,081

UNITED STATES PATENT OFFICE.

PIERRE ALEXANDRE BARBET, OF PARIS, FRANCE.

PROCESS OF CONTINUOUS SULPHONATION OF BENZENE, APPLICABLE TO IMPURE BENZENES.

Application filed April 23, 1917. Serial No. 163,898.

To all whom it may concern:

Be it known that I, PIERRE ALEXANDRE BARBET, citizen of the French Republic, residing at 5 Rue de l'Echelle, Paris, France, have invented certain new and useful Improvements in Processes of Continuous Sulphonation of Benzene, Applicable to Impure Benzenes, of which the following is a specification.

Benzene is easily attacked by heated sulphuric acid and still more easily by fuming sulphuric acid; and the combination or compound so formed (benzene sulphonic acid) may serve as a base for further transformations, particularly for the synthetic production of phenol.

Benzene is generally sulphonated by discontinuous operations in large cast iron boilers or stills which are closed and provided with a stirrer.

The circumstances have led to use for such a reaction impure benzenes, specially those which are extracted from the Borneo or Malaysia's gasolines, benzenes which hardly contain 50–55% of benzene, the remaining being an oil which cannot be sulphonated.

The presence of so important a quantity of gasoline or petroleum hydrocarbons does not prevent sulphonation of the benzene, but the same nevertheless constitutes a very great nuisance, on the one hand by the space it uselessly occupies within the sulphonating apparatus, whereby its daily productiveness will be lessened, and on the other hand by reason of the temperature which must be attained, which will cause the development of high pressures due to the vaporization of the petroleum hydrocarbons.

The present invention is a process whereby the said benzenes may be sulphonated in a continuous way.

The said process essentially consists in bringing in a continuous manner the benzene, either pure or charged with oil or other impurities, in the state of vapor into an intimate, methodical and sufficiently prolonged contact with fuming sulphuric acid, heated and constantly maintained at the desired temperature, the said acid being introduced in a continuous way and the benzene sulphonic acid so produced being abstracted also in a continuous manner.

The details of this process will be pointed out in the following description.

The apparatus has the general configuration of a continuous distilling column.

A indicates a column of plates provided with bubbling caps of any type. There are interposed therein some special plates called heating plates, wherein, for instance, heating coils are arranged on the said plates; these latter have for their object to maintain the temperature of the acid liquid at the desired degree. When desired, the bubbling plates may be further combined with heating coils extending between the rows of caps.

The fuming sulphuric acid is introduced in a continuous manner at the top of the column, preferably after the same is heated to the desired temperature by means of a heater D provided with a coil.

Benzene, whether pure or mixed with gasoline, is also introduced in a continuous way and controlled by the cock or valve R. The same becomes heated within the heat interchanger B by means of the heat contained in the sulphonated products which flow out of the lower part of the column A.

The same then passes through the heater-vaporizer C, wherein the benzene will be entirely vaporized.

The benzene will enter at the bottom of A, rise and pass through the whole of the plates in succession.

In the lower ones, the same will meet an acid which is already almost entirely transformed into benzene sulphonic acid and will finally saturate the said acid. Then progressively, as far as the vapour becomes poorer and poorer in benzene and consists of a larger proportion of oil, the same will bubble into acid which is increasingly capable of taking up benzene, and finally will in the upper plate pass through fresh acid, of the maximum density and sulphonating power.

Moreover, when it is considered that, by this system, the benzene vapour, at each unit of time, will only represent a relatively small quantity compared with the quantity of acid with which it is brought into association, it will be at once understood that the last portions of benzene will be retained.

The vapours of the unsulphonatable constituent of the material treated will flow through the acid and pass to the cooler E, then to the test-glass F and thence to the continuous purifier H, which is fed

with water by the cock or valve L and serves to retain the acid carried away (particularly a small quantity of sulphurous acid) and finally the gasoline freed from benzene and in a pure state will flow into the tank K.

The benzene sulphonic acid, which was formed during the gradual descent of the acid from plate to plate, will flow out of the pipe *b*, give up its heat to the entering benzene and finally flow into a tank G, wherein it will be cooled by means of a water-coil.

Such, is the whole operation.

As for the details of construction of the apparatus employed, the same may be varied within a certain limit.

With regard to the materials to be used in constructing the apparatus, it may be stated that experience has proved that cast-iron is very little corroded, because the acid is very concentrated. A column with cast-iron plates may, therefore, be used.

Plates of sheet metal lined with lead, or Volvic lava with leaden or porcelain caps, may also be utilized.

The process, whereby benzene may be sulphonated in a continuous manner, supplies the whole of the advantages which continuity offers in every industrial operation; more particularly, the same will secure a thorough homogeneity in the product obtained, a result which cannot be attained by the discontinuous operations.

Moreover, with the said process, the employment of mechanical agitations will be unnecessary, in fact, the necessary stirring will be produced in a perfect way by the intimate bubbling of the vapour through the sulphuric acid.

What I claim is:

1. A process of sulfonating benzene in a continuous manner, which comprises converting the benzene into a vaporized condition and bringing such vapor into continuous, intimate and methodical contact with heated concentrated sulfuric acid, supplying the heated sulfuric acid in a continuous manner, and removing the benzene sulfonic acid continuously.

2. A process of continuously sulfonating impure benzene mixed with oils which comprises converting the impure benzene into a vapor, bringing the vapor continuously into intimate contact with a continuous counter current of heated sulfuric acid, continuously removing the benzene sulfonic acid product, and separately therefrom continuously removing unsulfonated oils.

3. A process of continuously sulfonating impure benzene contained in admixture with unsulfonatable oils, which process comprises converting the impure benzene into a vapor, continuously bringing the said vapor into prolonged intimate contact with a continuous flowing hot current of concentrated sulfuric acid, continuously removing the liquid product containing the benzene sulfonic acid, and continuously removing and condensing the vapors of unsulfonated oils.

4. A continuous process of making sulfonic acids of benzene by causing vapors containing benzene to flow upwardly against a descending current of concentrated sulfuric acid in intimate and methodical contact therewith and continuously removing, in the liquid phase, the excess of sulfuric acid and the benzene sulfonic acids produced.

5. A continuous process of making a sulfonic acid compound of an aromatic hydrocarbon, which comprises causing an upwardly flowing current of vapors containing said aromatic hydrocarbon to meet and be brought into intimate and methodical contact with a downwardly flowing current of hot concentrated sulfuric acid and continuously drawing off the excess of sulfuric acid and the sulfonic acid compound produced.

6. A continuous process for the manufacture of a sulfonic acid of an aromatic hydrocarbon by causing the vapor of the hydrocarbon to come into contact with a descending current of sulfuric acid heated to a temperature above that at which the hydrocarbon boils, and continuously removing in the vapor phase any unsulfonated vaporizable material present, and also continuously removing in the liquid phase any excess of sulfuric acid and the aromatic sulfonic acid.

7. A continuous process for the manufacture of a sulfonic acid of benzene by causing the vapor of benzene to come into contact with a descending current of sulfuric acid, and continuously removing in the vapor phase any unsulfonated vaporizable material present, and also continuously removing in the liquid phase any excess of sulfuric acid and the benzene sulfonic acid.

8. A continuous process for the manufacture of a sulfonic acid of benzene by causing the vapor of benzene to come into contact with a descending current of sulfuric acid, heated and maintained at a temperature not below that at which benzene boils, and continuously removing in the vapor phase any unsulfonated vaporizable material present, and also continuously removing in the liquid phase any excess of sulfuric acid and the benzene sulfonic acid.

9. A continuous process for the manufacture of a sulfonic acid of benzene by causing the vapor of benzene to rise through a tower in which a stream of sulfuric acid is descending over obstructions to break and retard its fall, and continuously removing in the vapor phase any unsulfonated vaporizable material present, and also continuously removing in the liquid phase any excess of sulfuric acid and the benzene sulfonic acid.

10. A continuous process for the manu-

facture of a sulfonic acid of benzene by causing the vapor of benzene to rise through a tower in which a stream of sulfuric acid, heated and maintained at a temperature not below that at which benzene boils, is descending over obstructions to break and retard its fall, and continuously removing in the vapor phase any unsulfonated vaporizable material present, and also continuously removing in the liquid phase any excess of sulfuric acid and the benzene sulfonic acid.

11. A continuous process for the manufacture of sulfonic acids of benzene by causing the vapors of benzene to come into contact with a descending current of sulfuric acid, and continuously removing in the vapor phase the unacted on benzene and the water formed, and also continuously removing in the liquid phase the excess of sulfuric acid and the benzene sulfonic acids.

12. A continuous process for the manufacture of sulfonic acids of benzene by causing the vapors of benzene to come into contact with a descending current of sulfuric acid, heated and maintained at a temperature above that at which benzene boils, and continuously removing in the vapor phase the unacted on benzene and the water formed, and also continuously removing in the liquid phase the excess of sulfuric acid and the benzene sulfonic acids.

13. A continuous process for the manufacture of sulfonic acids of benzene by causing the vapors of benzene to rise through a tower in which a stream of sulfuric acid, heated and maintained at the temperature at which benzene boils, is descending over obstructions to break and retard its fall, and continuously removing in the vapor phase the unacted on benzene and the water formed, and also continuously removing in the liquid phase the excess of sulfuric acid and the benzene sulfonic acids.

14. A continuous process for the manufacture of sulfonic acids of aromatic hydrocarbons by causing the vapors of the hydrocarbon to mix with the vapors of sulfuric acid, and continuously removing in the vapor phase the unacted on aromatic hydrocarbons and the water formed, and also continuously removing in the liquid phase the excess of sulfuric acid and the aromatic sulfonic acids.

15. A continuous process for the manufacture of sulfonic acids of aromatic hydrocarbons by causing the vapors of the hydrocarbon to come into contact with a descending current of sulfuric acid, and continuously removing in the vapor phase the unacted on aromatic hydrocarbons and the water formed, and also continuously removing in the liquid phase the excess of sulfuric acid and the aromatic sulfonic acids.

16. A continuous process for the manufacture of sulfonic acids of aromatic hydrocarbons by causing the vapors of the hydrocarbon to come into contact with a descending current of sulfuric acid heated to the temperature at which the hydrocarbon boils and continuously removing in the vapor phase the unacted on aromatic hydrocarbons and the water formed, and also continuously removing in the liquid phase the excess of sulfuric acid and the aromatic sulfonic acids.

17. A continuous process for the manufacture of sulfonic acids of aromatic hydrocarbons by causing the vapors of the hydrocarbons to rise through a tower in which a stream of sulfuric acid heated to the temperature at which the hydrocarbon boils is descending over obstructions to break and retard its fall, and continuously removing in the vapor phase the unacted on aromatic hydrocarbons and the water formed, and also continuously removing in the liquid phase the excess of sulfonic acid and the aromatic sulfonic acids.

18. A continuous process for the manufacture of sulfonic acids of aromatic hydrocarbons by causing the vapors of the hydrocarbon to rise through a tower in which a stream of sulfuric acid heated to a temperature above that at which the hydrocarbon boils is descending over obstructions to break and retard its fall, and continuously removing in the vapor phase the unacted on aromatic hydrocarbons and the water formed, and also continuously removing in the liquid phase the excess of sulfuric acid and the aromatic sulfonic acids.

In testimony whereof I have signed my name to this specification.

PIERRE ALEXANDRE BARBET.

Witnesses:
LUCIEN PAILLARER,
CHAS. P. PRESSLY.