

# ALIEN PROPERTY CUSTODIAN

## SEPARATION PROCESS

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According to a known method organic compounds, in particular hydrocarbons, can be converted into compounds containing sulfur, oxygen and halogen by acting thereon with sulfur dioxide and halogen. The resulting compounds contain the said elements in the form of sulfohalide groups. The kind of compounds obtained and the number of sulfohalide groups depend on the nature of the initial material and on the manner in which the action of sulfur dioxide and halogen is carried out.

In the case of aliphatic hydrocarbons, the substances resulting from the treatment with sulfur dioxide and halogen are in most cases mixtures which contain unchanged starting material, and various sulfohalides, viz. products containing one sulfohalide group and others containing a plurality of such groups. These various sulfohalides are either employed as such or converted into sulfonic acids or their salts by hydrolysis. In view of the fact that the properties of the sulfohalides as well as of the hydrolyzed products vary frequently due to the position and the number of sulfohalide groups present therein, it is often desirable to separate the products from each other and in cases in which they contain unchanged initial material, and to separate it from the sulfohalides and to recover the same.

Particularly in the production of sulfonic acids from aliphatic hydrocarbons containing from between 12 to 16 or 18 carbon atoms by the treatment with sulfur dioxide and halogen and hydrolysis of the resulting sulfohalides it is necessary to remove unchanged hydrocarbons in order to avoid the formation of emulsions in consequence of the capillary activity of the sulfonic acids produced by the saponification of the sulfohalides with alkaline substances.

It is an object of the present invention to separate unchanged initial material from mixtures obtained by acting with sulfur dioxide and halogen on aliphatic hydrocarbons especially such containing from 12 to 18 carbon atoms.

It is a further object of our invention to separate from each other products having a higher content of sulfohalide groups from products containing less such groups.

The aim of this invention is reached by treating the starting mixtures with liquefied sulfur dioxide. The hydrocarbons serving as starting material for the treatment with sulfur dioxide and halogen are almost or entirely insoluble in liquid sulfur dioxide whereas the sulfohalides are more or less soluble therein. The solubility of

the sulfohalides in the liquid sulfur dioxide increases with the number of sulfohalide groups.

For example, a mixture obtained by acting with sulfur dioxide and chlorine on high-boiling liquid aliphatic hydrocarbons is stirred with liquefied sulfur dioxide whether at ordinary or even elevated temperature under pressure, or at a low temperature at its boiling point under atmospheric pressure or below. After standing for some time two layers are formed which may be easily separated from each other.

The separating action of liquefied sulfur dioxide, upon which the present process is based, is the better the lower is the temperature of working. Therefore, the process is advantageously carried out at relatively low temperature. Care must be taken, however, to choose the temperature not too low since the hydrocarbons used for the treatment with sulfur dioxide and halogen which accompany the resulting sulfohalides, frequently tend to become semi-solid or solid on cooling. This is particularly the case if higher molecular paraffin hydrocarbons are employed as starting material. In such cases the upper layer formed by the treatment with sulfur dioxide becomes a semi-solid mass which is difficult to work up further. If the process is performed, however, at higher temperature, in order to avoid such solidification, namely above the pourpoint of the hydrocarbons, the separating action of the liquefied sulfur dioxide becomes less satisfactory. In such cases the process can, nevertheless, be carried out to satisfaction if the treatment with the liquid sulfur dioxide is repeated once or several times.

Such repeated treatment can be avoided, however, by carrying out the process in the following manner, which may be called a two-stage-process. In a first stage, the initial mixture is treated with liquid sulfur dioxide at a temperature above the pourpoint of the unchanged hydrocarbons, and the resulting two layers are separated from each other. In a second stage, the bottom layer which contains the main quantity of sulfohalides is then cooled for itself or with an added amount of sulfur dioxide until two layers are again formed which are also separated from each other. By working in this manner, the solidification of the hydrocarbons is avoided, while, at the same time, the sulfur dioxide extract is enriched in sulfohalides. In order to cool the bottom layer obtained in the first stage the usual methods may be employed but advantageously the cooling is effected internally by allowing the liquefied sulfur dioxide to vaporize

to such an extent that the desired temperature is reached. For this purpose a corresponding excess of liquid sulfur dioxide is employed so that after the vaporization of the part effecting the cooling sufficient sulfur dioxide remains dissolved behind to keep the sulfohalides. If necessary, the second stage may be repeated once or several times.

A particularly advantageous manner of carrying out the process consists in performing it continuously in a counter current by employing a column with fillers. This method is of particular value in cases in which the starting mixture contains appreciable amounts of unchanged hydrocarbons, as is the case if the treatment of the hydrocarbons, with sulfur dioxide and halogen is only carried on to such an extent that about half or less thereof is converted into sulfohalides.

Further particulars of our invention will appear hereinafter in the following Examples which illustrate the invention which is, however, not limited thereto. The parts are by weight.

#### Example 1

100 parts of a product obtained by acting with sulfur dioxide and chlorine on a mixture of aliphatic hydrocarbons, boiling between 240 and 360° C which have been produced by the catalytic hydrogenation of carbon monoxide, and containing as an average 4.87 per cent of sulfur, 7.30 per cent of chlorine, whereof 5.54 per cent are saponifiable, are stirred for some time while adding 300 parts of liquid sulfur dioxide. After standing for a short time two layers are formed. The bottom layer is a completely clear solution which contains the sulfochloride, whereas the hydrocarbons separate above it as an undissolved semisolid mass. By evaporating the sulfur dioxide which may be reliquefied and used again, a product is obtained which contains 12.40 per cent of saponifiable chlorine and which when saponified yields a product possessing high foaming power and giving with water a clear solution.

#### Example 2

200 parts of a reaction product obtained in a manner analogous to that described in Example 1 which contains 11.09 per cent of sulfur, 15.60 per cent of total chlorine and 13.40 per cent of saponifiable chlorine, are stirred with 400 parts of benzine, a sludgy dark-colored bottom layer being formed which is separated, whereafter the benzine is completely removed by distillation. The residue still contains 11.72 per cent of saponifiable chlorine. 200 parts of the product thus purified are then stirred with 450 parts of liquid sulfur dioxide, the mixture being then further treated as in the foregoing Example. There are obtained 25 parts of hydrocarbons and 174 parts of a sulfochloride, the content of saponifiable chlorine of which is 13.14 per cent.

The process according to the present invention may also be applied to a product containing sulfur, oxygen and chlorine obtained by acting with sulfur dioxide and chlorine on kerosene.

#### Example 3

2000 parts of a mixture consisting of about equal parts of sulfohalides and neutral hydrocarbons which is obtained by acting on a mixture of liquid hydrocarbons having an average molecular weight of 210 with sulfur dioxide and chlorine, are mixed in a closed vessel with the double amount by weight of liquid sulfur dioxide. The mixture is stirred at 15° C for some time and then allowed to stand until the formation of two layers is completed. The upper layer consists of 1250 parts. It contains 195 parts of sulfur dioxide, 211 parts of sulfohalide and 844 parts of unchanged hydrocarbons, corresponding to 1055 parts of a 20 per cent solution of sulfohalide in unchanged hydrocarbons. The amount of sulfohalide corresponds to 20 per cent, the amount of unchanged hydrocarbons to 80 per cent of the originally present quantity. The bottom layer consists of 4065 parts, namely 3205 parts of sulfur dioxide, 172 parts of unchanged hydrocarbons and 688 parts of sulfochloride corresponding to 860 parts of a 20 per cent solution of hydrocarbons in sulfochloride. After having separated the two layers, 3 per cent of the sulfur dioxide of the bottom layer are allowed to vaporize. The bottom layer is cooled thereby to 10° below zero C and two layers are again formed. In spite of the remarkable cooling and the high content of hydrocarbons, the upper layer does not solidify but remains liquid. After separating it and evaporating the sulfur dioxide contained therein it consists of 205 parts of a mixture containing 86 parts of sulfohalide and 119 parts of hydrocarbons. Calculated on the originally present amount this means 9 per cent of sulfohalide and 12 per cent of hydrocarbons. The bottom layer consists, after the vaporization of the sulfur dioxide, of 655 parts, namely 589 parts of sulfohalide and 66 parts of hydrocarbons. This layer consists consequently of a 10 per cent solution of hydrocarbons in sulfohalide; calculated on the originally present amount it contains 59 per cent of sulfohalide and 7 per cent of hydrocarbons.

The upper layer from the first stage is preferably used once more for the treatment with halogen and sulfur dioxide. The upper layer of the second stage is mixed with fresh initial mixture and simultaneously with it subjected to the separation according to this invention.

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