

# ALIEN PROPERTY CUSTODIAN

## PROCESS FOR OBTAINING CRYSTALLINE MATERIALS FROM OILS

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This invention relates to a process for obtaining crystalline material from oils, and it has particular relation to the recovery of crystalline compounds from tar oils, particularly coal tar oils.

According to known methods, tars, for instance coal tar, are subjected to fractional distillation in order to obtain oil fractions rich in the crystalline compounds to be recovered. The recovery of these compounds is then effected by cooling said fractions to crystallization temperature, and separating the crystals formed from the bulk of the non crystallizable oils by filtering with suction or centrifuging. If sufficiently pure crystals cannot be obtained by these steps, the non crystallizable material must be separated from the crystals by squeezing off the oil, for instance in a high pressure press under a pressure up to 300 atm. This treatment, however, is not practicable or causes difficulties in some cases, owing to the high viscosity of the oily constituents or the smeary nature of the crystals. In such cases, the viscosity of the oil can be reduced by the addition of solvents, or the oil-containing crystals, after separation from the bulk of the oil, can be purified by dissolving and recrystallizing them by means of a suitable solvent. The use of solvents, however, causes an essential reduction in the yield of the crystals, particularly if the crystals are easily soluble. Moreover, losses of the solvent are unavoidable, and essentially raise the costs of the process.

It has now been found that the above mentioned drawbacks can be avoided, and crystals, which are essentially free from or poor in oil, can be obtained from oils, by proceeding as follows.

The oil fraction containing crystallizable compounds, for instance an oil obtained by fractional distillation of coal tar, is introduced into and mixed with a hot aqueous emulsion of an organic solvent, for said oil, the mixture obtained is cooled to crystallization temperature, and the crystals formed are separated from the emulsion. It has been found that the presence of water in said mixture causes slow crystallization of the crystallizable compounds contained in the oil. Moreover, the presence of water reduces the dissolution of the crystalline substance and losses caused by such dissolution. Finally, as the volume of the liquid is essentially increased by the addition of water, the crystals remain in a loose condition in the liquid, and can easily be separated from it.

The present invention may be used, for instance, for the recovery of crystalline substances

from oils which are obtained by fractional distillation of coal tar or coal tar oils and, owing to the formation of crystals, are semiliquid or solid at ordinary room temperatures, or consist of high-boiling substances which are highly viscous and not fluid at said temperatures. In carrying out the invention, the tar oil is heated until it forms an essentially homogeneous liquid, and is then introduced under stirring into a hot emulsion, which contains water and an organic solvent and preferably an emulsifying or wetting agent. The organic solvent is used for taking up the oily constituents of the tar oil, and may be a coal tar oil or another solvent, which is essentially not soluble in water, and can homogeneously be mixed with said oily constituents. Distillation products of coal tar, brown coal tar, carbonization tar or petroleum, may, for instance, be used. Other suitable solvents and mixtures of several solvents may also be used. The wetting or emulsifying agent influences the surface tension of the solvent and the oil to be treated and thus facilitates the thorough mixing of water, oil and crystalline substance. Soaps, for instance alkali soaps of colophony, naphthenic acid soaps, fatty acid soaps, salts of sulfo acids, or other wetting or emulsifying agents or their mixtures, may be used. Our present invention can also be carried out without employing such agents, as an intimate mixing of the above mentioned individual components may be effected by mechanical stirring alone. However, the use of emulsifying or wetting agents essentially facilitates the carrying out of the invention. The emulsifying or wetting agent may preferably be added to the solvent before mixing it with water, or may be formed by partial or complete saponification of saponifiable components contained in the solvent, which is then mixed and emulsified with the necessary amount of water. 20 parts of a tar oils solvent, to which a rosin soap has been added, may, for instance, be mixed and emulsified with 80 parts of water.

According to another embodiment of our invention a part of the solvent may be added to the oil containing the crystallizable substance to be recovered, and the other part of the solvent mixed and emulsified with water. Thereby, two different solvents may be used, one of which is used for diluting the oil containing the crystallizable substance to be recovered, and the other, to which an emulsifying or wetting agent may be added, for preparing the aqueous emulsion.

In carrying out the present invention, the crystals to be obtained are formed and separated

from the oil during cooling the mixture of starting material and aqueous emulsion of the solvent under stirring. The crystals thus formed can be obtained essentially free from oil, by separating them from the liquid mixture. They can be separated from the cooled mixture, for instance by filtering with suction or centrifuging, and can be washed with water in order to remove adhering particles of the emulsion. The residual oily parts of the starting material are taken up by the droplets of solvent which are finely distributed in the emulsion.

*Example 1.*—300 parts by weight of drained naphthalene are heated to 100°C and introduced under stirring into an emulsion obtained from 360 parts by weight of water and 90 parts by weight of a coal tar oil, which has a boiling range of 200° to 300° C and contains 20 parts by weight of sodium resin soap in solution. This emulsion is heated to 95°C before mixing it with the naphthalene containing material. The mixture is cooled under constant stirring to 30°C. Thereby, crystallization takes place, and the crystals are then separated from the liquid by filtering with suction. The crystals are then washed with water and centrifuged in order to separate them from water. Thereby 240 parts by weight of a naphthalene having a solidification point of 79,0°C are obtained. The naphthalene thus obtained contains only traces of water and corresponds in its quality to a hot-pressed naphthalene.

A change in the temperature, to which the mixture is cooled, for instance to 50°C, or 20°C or less, causes corresponding change in the yield and solidification point of naphthalene, in a manner similar to that which occurs in the customary pressing method by changing the pressure used and the duration of pressing.

*Example 2.*—300 parts by weight of a coal tar oil which boils between 293° and 309°C, and becomes clear when heated to 73°C are heated to 100°C, and treated, as described in Example 1, with an emulsion which has previously been heated to 95°C, obtained from 400 parts by weight of water and 100 parts by weight of a coal tar oil, which has a boiling range of 200° to 300°C and contains 20 parts by weight of sodium resin soap. By cooling the mixture under stirring to 25°C, filtering with suction, washing with water and centrifuging, 78,9 parts by weight of crystals are obtained. These crystals are free from water and contain only 6% of oil. This oil does not affect the further working up of these crystals which consist essentially of diphenylene-oxide, fluorene, and phenanthrene.

Instead of treating the above mentioned coal tar oil boiling between 293° and 309° C, the solid residue obtained by cooling this oil to ordinary room temperature and then subjecting it to filtering with suction, may also be treated according to our present invention. For instance, 200 parts by weight of such residue consisting of crystallized substances and oils are heated to 120° C and then mixed under stirring with an emulsion, which has previously been heated to 95°C, obtained from 200 parts by weight of water and 90 parts by weight of a coal tar oil which has a boiling range of 200–300° C and contains 20 parts by weight of sodium rosin soap. After cooling and filtering with suction a mixture of crystals is obtained which after being washed with water is essentially free from oil. The crystals are freed from water by centrifuging and contain then about 3% of oil which is much less than the

oil contents of crystals obtained under similar conditions by pressing.

*Example 3.*—2000 parts by weight of a coal tar oil which boils between 310° and 330°C and becomes clear when heated to 120°C, are heated to 120°C and mixed under stirring with an emulsion which has previously been heated to 80°C obtained from 1600 parts by weight of water and 400 parts by weight of a tar oil which boils between 200° and 300°C and contains 20 parts by weight of sodium rosin soap in solution. The mixture obtained is cooled under stirring to 25° C and subjected to filtering with suction; the solid residue is washed with water and centrifuged. Thereby 1290 parts by weight of crystals are obtained which are free from water and contain 4–5% of oil, i. e. essentially less than contained in a product which is obtained under similar conditions by pressing.

*Example 4.*—300 parts by weight of a pyrene containing coal tar oil which boils between 382° and 394° C and becomes clear when heated to 76°C are diluted with 60 parts by weight of gas oil boiling between 220 and 360° C and heated to 100°C. The oil mixture thus obtained is introduced into a liquid of 100° C obtained from 100 parts by weight of liquid cresol soap, and 200 parts by weight of water. The liquid cresol soap may be obtained, for instance, by dissolving cresol in sodium-hydroxyde or potassium hydroxyde solution as described for example in pharmaceutical compendiums. The mixture is cooled under constant stirring to 25°C after which it is mixed by stirring with a further amount of 200 parts by weight of water. The crystals formed are separated from the liquid by filtering with suction and washed with about 500 parts by weight of water. Thereby 165,9 parts by weight of crystals are obtained. The crystals contain only 2,5% of oil and traces of water.

*Example 5.*—300 parts by weight of the coal tar oil used in accordance with Example 4, are mixed with 60 parts by weight of a coal tar oil which boils between 180° and 210° C. The mixture is heated to 100° C and introduced under thorough stirring into a 100° C hot solution of 75 parts by weight of sodium soap of naphthenic acid and 75 parts by weight of water. The mixture is cooled under stirring to 35°C; it is then mixed by stirring with a further amount of 300 parts by weight of water. By further cooling to 25° C, filtering with suction and washing with water, 152,1 parts by weight of crystals are obtained which are free from water and contain only 1% of oil.

The process of our present invention can also be used for obtaining crystallizable substances from other oils essentially in the same manner as described in the above examples.

The amounts of the solvent, wetting or emulsifying agents and of water, to be used depend on the properties of the starting material which contains the crystallizable compounds to be obtained. The carrying out of the present process requires the use of sufficient amounts of the substances to be added. Sufficient water should be added in order to obtain a mixture which can be stirred thoroughly even at lower temperatures, and sufficient solvent should be present for taking up the oily portions contained in the mixture. We prefer to use for preparing the emulsion 20–30 parts by weight of a solvent containing a wetting or emulsifying agent, and 70 to 80 parts by weight of water. For carrying out the process of our present invention we also prefer

to use an amount of this emulsion, which, after mixing with the oil to be treated, will still be of the oil-in-water type. This facilitates the washing of the separated crystals with water.

Owing to the presence of water, the above described emulsions cannot be heated to temperatures over 100° C. It is, therefore, not advisable to heat the oils to be treated to temperatures essentially higher than those disclosed in the above examples. It is, however, advantageous to reach the temperature of 100°C during mixing the oil with the emulsion in order to obtain a slow crystallization. The cooling may be performed in any suitable manner with or without artificial cooling of the stirring apparatus. The slower the cooling is performed, the better the crystals can develop. The separation of crystals from the liquid can be carried out in any suitable device, for instance by means of a suction filter or

by treating the mixture of crystals and liquid in a centrifuge. The washing of the crystals can take place, for instance in a suction filter or in a centrifuge.

5 In our present specification and claims "crystallization temperatures" it is to be understood are those at which the crystallizable substances to be obtained from the oils separate from said oils in the form of crystals, whereas the oils and solvents used, and the water present in the emulsion, still remain liquid. The term "solvent" 10 used in the present specification and claims denotes liquids which are essentially not soluble in water and can be mixed homogeneously with the oils from which the crystallizable substances 15 have been separated.

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