

UNITED STATES PATENT OFFICE.

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HYDROCARBON SOAP AND PROCESS OF MAKING SAME.

1,040,708.

Specification of Letters Patent.

Patented Oct. 8, 1912.

No Drawing.

Application filed January 21, 1911. Serial No. 603,902.

To all whom it may concern:

Be it known that we, PAUL GEORG LIST, doctor of philosophy, chemist, and resident of Tübingen, Germany, with post-office address Naukterstrasse No. 60, and GEORG SCHMIDT, chemist, and resident of Offenbach-on-the-Main, Germany, with post-office address Buchrainweg 4, both subjects of the German Emperor, have invented new and useful Improvements in Hydrocarbon Soap and Processes of Making Same, of which the following is a specification.

The object of our present invention is the production of a soap containing aromatic hydrocarbons in a perfectly soluble condition, such soap being soluble not only in fresh water, but also in water containing salt in solution, *e. g.* sodium-chlorid up to 4 or 5%. Our new soap can also be used with sea water, provided that the latter has been treated with a suitable quantity of slaked lime, caustic alkali or alkali carbonate, as for instance, sodium carbonate.

It is old to use hydrocarbons as filling material for hard and soft soaps. German and English patents describe several processes which consist in bringing together at an elevated temperature hydrocarbons with concentrated or diluted soap material. It is also old to produce carnauba petroleum soaps which are soluble in water. This is explained by their inventors by the fact that the myricyl alcohol, released when the carnauba wax is split up, dissolves the petroleum and keeps it dissolved in the soap solution. The myricyl alcohol, accordingly, fulfils the same purpose as the addition of alcohol, and the presence of phenols, in the process described in German Patent No. 52129. Aside from these special instances where the solubility results from the myricyl alcohol, ethyl alcohol, and phenols, only such hydrocarbon soaps soluble in water have been heretofore known as were manufactured with the aid of chlorin substitution products of methane and ethane. Thus for instance, carbon tetrachlorid and perchlorethylene readily combine with ricinoleic soaps; all that is necessary is to permit the components to react at an elevated temperature and in the presence of a small amount of water, and a soap soluble in water will soon be obtained. These soaps which contain chlorin substitution products

of the methane or ethane groups made soluble in water, have the great advantage over soaps heretofore produced containing hydrocarbons of the benzol group as filling material, *i. e.* in an insoluble form, that the clear soap lye can more thoroughly penetrate the articles to be washed, and that the solvent action of the hydrocarbons, made soluble in water, is much more effective. Experience shows, however, that these soaps sometimes give a yellow tinge to the articles washed which is explained by the fact that during transportation the carbon tetrachlorid is sometimes accidentally decomposed, and iron salts are formed which afterward enter into the soap.

Benzol and its homologues have not been employed heretofore in the same manner as such chlorin substitution products of ethane and methane, because no one had succeeded in transmuting, for instance, ortho- or meta-xylol, pseudo-cumol, or other homologous substances, into a form in which they were soluble in water. These hydrocarbons have been used in the manufacture of soaps only as filling material; consequently only an emulsion, but no pure homogeneous, clear solution of the two components, could be obtained by solution in water.

The surprising discovery has been made by us that it is easy to convert toluol, xylol and pseu-cumol with fatty acid salts of alkalis into a product soluble in water if said hydrocarbons are allowed thoroughly to react for a comparatively long time while being stirred with a hot and concentrated soap material, or with fats or fatty acids to which alkali and some carbonate of an alkali has been added. In the beginning only a physical combination, *i. e.* an emulsion, takes place, and only after the mixture has been stirred or agitated, and simultaneously heated, is the desired new product obtained. The duration of the process and the temperature must be regulated accordingly to the nature of the fats used.

With some soaps, for instance, those made of palm oil, tallow, etc., a higher temperature is necessary while for oleic acid and castor oil a lower temperature is sufficient.

The important feature of my process is to stir the concentrated mixture thoroughly for a sufficient length of time, in some cases for ten hours. As the reaction proceeds the

product becomes more and more soluble in water and possesses the surprising characteristics that, upon the addition of common salt even up to 4 and 5%, it is not precipitated out of the soap solution. The new product obtained by the reaction may also be directly dissolved without producing turbidity, in water containing 4-5% salt, as well as in water taken from the North Sea which has been treated with carbonate of soda; it also remains dissolved in the salt water solution if this is allowed to cool down to 20-30° C., while all hard and soft soap is immediately precipitated from solution by the addition of salt. This solubility in salt water is the essential characteristic and it proves the thorough combination of the hydrocarbon with the soap, *i. e.* that the hydrocarbon has become soluble in water. This result is very surprising and could not have been foreseen. By following the processes described in the British Patents 19732 of 1893, 300 of 1879, and 8982 of 1909 only such soaps are obtained as separate out toluol, xylol or benzol from the soap solution, that is to say soap which can never produce a clear solution. The reason for this is that an excess of water is employed in their manufacture, and that the mixture is not stirred at an elevated temperature for a sufficient length of time. A combination of hydrocarbons and soap can never take place under these circumstances, and thus the soaps obtained according to the directions given in said British patents are not soluble either in water or in a 4-5% common salt solution in water. If such a soap is dissolved in a hot solution of salt in water, a curdy precipitate of the entire soap takes place immediately; this is the reason why these soaps are absolutely useless for technical purposes where salt water is used.

The soaps made according to the new process besides being soluble in salt water, possess the further property of having considerably smaller conductivity for electricity. The determination of their conductivity proves that a complete combination between the hydrocarbons and the fatty alkali acids has really taken place. The conductivity of a solution of pure sodium oxid soap is not affected by the subsequent addition of hydrocarbon, for instance of xylol. The conductivity of a solution of soaps containing hydrocarbons in a combined state is considerably smaller, and the only explanation for this is that a combination has taken place between the hydrocarbon and the anion (the fatty acid, radical) whereby said anion is made less movable as a result of the increase in complexity thereof. The determination of the conductivity of potash soap containing combined hydrocarbon made according to the present process, as

compared with that of ordinary potash soaps (of the same fatty substances), and as compared with that of such soaps after free hydrocarbon has been added, shows exactly the same results; the conductivity of combined hydrocarbon soaps is considerably less than the conductivity of ordinary potash soaps, and also considerably less than the conductivity of a mixture of potash soaps, hydrocarbon and water, (*e. g.* an emulsion). This shows that also in potash soaps containing combined hydrocarbon, the hydrocarbon is combined with the anion of the fatty acid, the result of which is that the new soap is soluble in water and in salt water.

The following examples will serve to illustrate the invention:

Example 1: 250 kg. of palm oil and other fats and oils as are used for the manufacture of hard soaps are saponified with a sufficient amount of sodium carbonate lye and a solution containing 5% caustic potash and salted out; thereupon the resulting soap is thoroughly stirred for several hours at a temperature of from 60 to 100° C. together with 100 kg. orthoxylol and some potash until a test portion of the soap proves to be completely soluble in water and is no longer precipitated by the addition of from 4 to 5% of common salt.

Example 2: 400 kg. oleic acid or ricinoleic acid, or of a mixture of oleic acid and ricinoleic acid, 250 kg. potash lye of 40° Bé. to which some potash has been added, and 200 kg. meta-xylol or solvent naphtha are allowed to react on each other until saponification takes place and until the combination of the hydrocarbon with the anion of the fatty acid is shown by the resulting solubility in salt water. The heat generated by the reaction is sufficient to effect this combination. This process can be carried out in about 6 hours.

Example 3: 70 kg. of light soft soap made of tallow, palm oil, castor oil, cotton seed oil, or of a mixture of these oils, together with 30 kg. of pseudo-cumol and some potash are heated while being stirred, for several hours, the temperature being increased from 30 to 40° to from 50 to 60° and finally to from 80 to 110° until a paste like homogeneous substance is obtained.

As soon as the solubility in salt water has been determined—which means that the combination has taken place—from 50 to 70 kg. of a weak potash lye may be added, whereby a homogeneous product similar to olive oil is obtained, which product will not decompose, and which will remain soluble if mixed with water or with salt water containing from 4 to 5% of salt. The original paste-like product, after the combination has been completed, may also be thoroughly mixed with from 100 to 200 kg. of calcined sodium carbonate until a dry soap powder

is obtained. This soap powder likewise is completely soluble in water, and in salt water containing from 4 to 5% of common salt.

3 The fact that these hydrocarbon soaps are soluble in salt water makes it possible to use sea water for cleaning purposes, as the hydrocarbon soaps are completely soluble in sea water, if some sodium carbonate is added.

10 This is a great technical advantage, for heretofore sailors on the high seas could dissolve soap only by using fresh water which had been carried along or by using expensive condensed water.

15 The following process is given as an illustration: For the purpose of cleaning soiled linen, soiled fabrics or other objects, with salt water, from 4 to 10 kg. of liquid or solid hydrocarbon soap, or a corresponding quantity of hydrocarbon soap powder, are dissolved to a clear solution in about 200 liters of salt water containing from 3 to 5% of salt. In the solution thus prepared the objects to be cleaned are stirred for some time, and are then washed in the usual manner. This soap solution shows the same properties as the ordinary soap solution made from river or well water. In a very short time this salty soap solution completely removes all dirt, especially resins, fats and oil spots.

If ordinary sea water is to be used for preparing a soap solution, a sufficient quantity of lime, alkali or alkali carbonate must be added to the sea water, for instance 2 kg. of sodium carbonate to 200 liters of sea water, and the solution then boiled. To the solution thus prepared which may be filtered if necessary from 4 to 10 kg. of combined hydrocarbon soap are added. The entirely clear soap solution is then used for cleaning linen and the like.

It is also to be noted that the soaps made according to this new process, after the concentrated alkali soap has been combined with the hydrocarbon, may be diluted with water to any desired extent and may then be used as soaps, oils, etc. for use in boring, cutting, or otherwise machining metals.

50 In the metal industry for use in boring, turning, planing, milling and cutting off metal pieces only aqueous solutions of soaps or oils soluble in water have been used heretofore as cooling agents. This method of working, however, had the disadvantage that this aqueous soap solution which has only a limited capacity of dissolving fats, smears the tools, blunting them prematurely and assisting in the formation of rust. It has been found that the addition of hydrocarbon to such soaps or oils, as are used as cooling agents, is of great advantage, provided a process is used, whereby these products contain the hydrocarbon in a form in which they are soluble in water. The solu-

tions remain more homogeneous and show a higher efficiency. The smearing of the tools is avoided, because the hydrocarbon dissolved in water holds the fatty and dirty matter in solution. The tools are less affected, hold their edge and do not rust. A soap particularly suited for this use is that obtained by following the process explained in Example 3.

In the following claims: the expression "soapy material" includes either a ready formed soap or the ingredients which will produce soap. The expression "excluding water as much as possible" means that only sufficient water is present for the solution of the substances present, and for the saponification.

The expression "completely soluble" means that the product, on treatment with water produce a clear solution, as distinguished from an emulsion or milky liquid. Milkiness or turbidity of a liquid indicates that there is some substance present which is not in solution, but is usually carried as a substance in suspension or as an emulsion.

What we claim is:

1. A process of making a soap containing soluble aromatic hydrocarbons, which process comprises reacting upon such a hydrocarbon with a soapy material, under the joint action of heat and agitation, while excluding water as much as possible, until a product completely soluble in water is produced, substantially as described.

2. The process of making a soap containing soluble aromatic hydrocarbons, which process comprises combining such a hydrocarbon with fat and alkali lye at an elevated temperature, while excluding water as much as possible during the reaction, and producing a product completely soluble in water as described.

3. The process of making a soap containing soluble aromatic hydrocarbons, which process comprises combining such a hydrocarbon with oleic acid and caustic potash lye at an elevated temperature, while excluding water as much as possible, and producing a product completely soluble in water.

4. The process of making a soap containing soluble aromatic hydrocarbons, which process comprises combining xylol with a soapy material while excluding water as much as possible, and producing a product completely soluble in water, substantially as described.

5. The process of making a soap containing soluble aromatic hydrocarbons, which process comprises combining solvent naphtha with a soapy material while excluding water as much as possible during the process of combination, and producing a product completely soluble in water, substantially as described.

6. The process of making a soap contain-

ing soluble aromatic hydrocarbons which process comprises combining solvent naphtha with an oleic acid and caustic potash lye, while excluding water as much as possible during the process of combination, and producing a product completely soluble in water, substantially as described.

7. A process of making a perfectly soluble soap containing hydrocarbons of the aromatic series, which process comprises reacting upon a soap with said hydrocarbons under such conditions as to produce a product completely soluble in water containing up to 5% of sodium chlorid in solution.

8. A process of making a perfectly soluble soap containing hydrocarbons of the aromatic series, which process comprises reacting upon a soap with said hydrocarbons while heating and agitating the reacting ingredients until a product completely soluble in water containing up to 5% of sodium chlorid in solution is obtained.

9. A process of making a perfectly soluble soap containing hydrocarbons of the aromatic series, which process comprises reacting upon a soap with said hydrocarbons while heating and agitating the reacting ingredients until a product completely soluble in water containing 4 to 5% of sodium chlorid in solution is obtained.

10. Process of making soaps containing hydrocarbons of the benzol series in a form in which they are soluble in water, which process consists in causing these hydrocarbons to react while being stirred and at an elevated temperature upon a soapy material until a test portion of the product obtained by this reaction becomes clearly soluble in water and does not precipitate if from 4 to 5% of common salt are added.

11. As a new article of manufacture, a soap containing hydrocarbons of the aromatic series, said product being completely

soluble in pure water, and in water containing up to 5% of sodium chlorid.

12. As a new article of manufacture a soap containing hydrocarbons of the aromatic series, the solution of said product in water having a considerably smaller conductivity for electricity than a solution of pure soap of the same molar concentration.

13. As a new article of manufacture, a soap containing the hydrocarbons of coal-tar, soluble in water, which may be obtained by combining a hydrocarbon of coal-tar with a soapy material and excluding water as much as possible during the process of combination, said products being soluble in fresh water and in salt solutions as well as in sea water, when the latter has been previously heated together with sodium carbonate, said products being adapted for cleaning soiled linen, textile fabrics and the like.

14. As a new article of manufacture, a soap containing hydrocarbon, which product may be obtained by combining solvent naphtha with oleic acid and caustic potash lye at an elevated temperature while excluding water as much as possible during the reaction, said product being soluble in fresh water and in salt solutions as well as in sea water, when the latter has been previously heated together with sodium carbonate, said product being adapted for cleaning soiled linen, textile fabrics and the like.

In testimony, that we claim the foregoing as our invention, we have signed our names in presence of two witnesses, this second day of January 1911.

PAUL GEORG LIST.
GEORG SCHMIDT.

Witnesses:

EVA SATTLER,
JEAN GRUND.