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METHOD OF ISOLATING CONSTITUENTS OF COMPLEX MIXTURES

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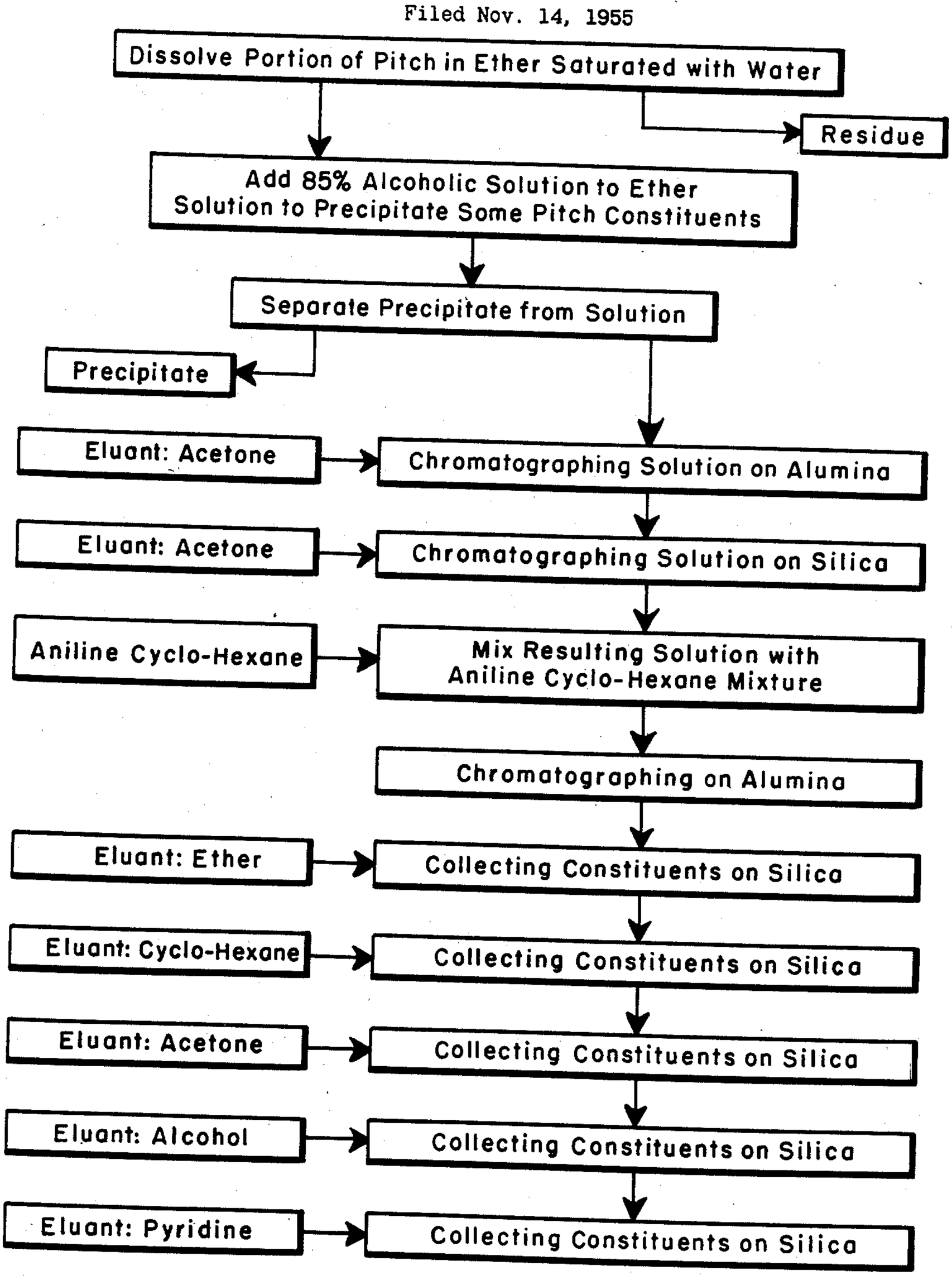

INVENTORS.
Rene Paris
Jean-Charles Pariaud
Paul Bonny
Alexis Dufour
BY Webb, Mackey + Burden
THEIR ATTORNEYS

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METHOD OF ISOLATING CONSTITUENTS OF COMPLEX MIXTURES

René Paris and Jean-Charles Pariaud, Lyon, Paul Bonny, Venthon par Albertville, and Alexis Dufour, Les Loges-en-Josas, France, assignors to Societe d'Electro-Chimie d'Electro-Metallurgie et des Acieries Electriques d'Ugine, Paris, France, a corporation of France

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1 Claim. (Cl. 208—45)

The present invention relates to a method of isolating in the pure state the constituents of complex mixtures of organic substances and especially of pitches such as coal pitch, for example.

Coal pitch constitutes a complex mixture of a number of compounds, the nature and the percentage content of which depend on the conditions under which the pitch is obtained. None of the works published up to the present time, concerning the analysis of these pitches and their treatment with a view to the isolation of fractions or of definite compounds in the more or less pure state, provides any systematic method of fractionation which enables all the chemical species which constitute the whole of the pitch studied to be isolated in succession and in the pure state. This is the reason why no one has been able to prepare up to the present time any complete balance sheet, either quantitative or even qualitative, of the constituents of a given pitch.

The standard techniques of proximate analysis are in fact ineffective on the initial mixture because of the mixture's great complexity. If the analysis is attemped in the cold state, the method is totally useless; if the work is carried out in the hot state, there is a risk of destroying the very components which it is desired to determine.

The present invention avoids these difficulties. It has for its object a practical method of treatment of coal pitch, by means of which it is possible to isolate all its constituents in the pure state, either for the purposes of a qualitative and quantitative analysis, or for the purpose of the preparation of chemical species, either new or already known, from the pitch considered as a raw material.

In the drawing we have illustrated a present preferred embodiment of our invention in which is shown a flow chart of the process.

The present method consists essentially in carrying out a preliminary fractionation of the initial complex mixture, either by means of appropriate successive solvents, or by a fractional precipitation of a solution as complete as possible of this initial mixture, in order that each fraction may only contain a number of constituents sufficiently restricted in number to allow the use of standard techniques of proximate analysis which cannot be applied to the initial mixture, and then to proceed effectively to apply the said techniques to the various fractions.

In the case of a fractionation by means of a number of successive solvents, these solvents are chosen in such manner that the constituents of the pitch collect in them according to a decreasing order of solubility. A beginning is made, by means of a fairly weak solvent, by dissolving the most soluble constituents; then the constituents which are a little less soluble are dissolved by means of a slightly stronger solvent, and so on. Certain constituents which are not wholly dissolved in one single fraction may be found in two successive fractions.

If so required, the various solutions may also be fractionated with several immiscible solvents.

An alternative method consists in taking a solution, which is as complete as possible, of the initial complex mixture and in precipitating the constituents of this solution in the order of their increasing solubility.

Although it should always be considered that the solubilities of substances in mixtures are clearly different from their solubilities in the pure state in a given solvent, experience has shown that the characteritics of solubility are in relation to the size and the molecular complexity of the constituents.

The fractions of the pitch resulting from the sorting process in accordance with the invention are then subjected to chromatographic separations by employing different adsorbents, or by alternating these adsorbents, or by using a whole series of eluants of increasing power, or finally by combining all these alternative methods of chromatography. Use may also be made of treatment by electrophoresis, fractional molecular sublimation, and in a general way, of all the methods of proximate analysis which can be carried out at ordinary temperatures, in an inert atmosphere and protected from light, in order to avoid all thermal, oxidizing or photo-chemical change in the constituents of the pitch.

This method of fractionation and isolation of the pure constituents of a complex mixture is not limited to coal pitches, but may be applied with the same success to petroleum pitches, to asphalts and, still more generally, to any mixture which comprises a large number of organic substances.

The examples given below without any implied limitation, will make it clearly understood how the method which forms the object of the invention may be applied.

Example 1.—Separation of the constituents of the most soluble fraction of a pitch

Operation was commenced by isolating a fraction which represented one-tenth of the weight of the initial pitch. To this end, the pitch was first of all treated with 30 parts of ether saturated with water, which dissolved 40% of the product. This first solution was then precipitated by an 85% solution of alcohol; there then remained 20% of the initial weight in solution. This second solution was first of all chromatographed on alumina, then on silica, utilising each time acetone as an eluant. There was thus obtained a third solution which, when stirred with an aniline-cyclo-hexane mixture enables the constituents corresponding to one-tenth of the initial pitch to be collected in the layer of aniline.

The chromatography on alumina was effective when carried out on this third solution.

Each of the fractions collected was treated on silica, using successively as eluants ether, cyclo-hexane, acetone, alcohol and pyridine. There were finally obtained 62 crystalline species with well-defined melting points and representing pure constituents. There still remained a certain number of complex fractions. Amongst the crystalline species were found chrysene and fluorene, which had already been extracted from coal pitch by methods other than that of the present invention. Others, such as trioxy-naphthalenes, the ortho and meta-hydroxy-benzoic acids, xanthene and picolinic acid on the other hand, had never been indicated as constituents of pitch.

Example 2.—Separation of the less soluble constituents of pitch

The powdered pitch was treated to total extraction by 20 parts of pyridine. The residue, which was about 15% of the total pitch, proved to be quite insoluble in all known solvents. This residue is moreover not pure carbon and its existence had never previously been proved.

The addition of a very small quantity of water to the pyridine solution S_1 gave rise to the precipitation P_1 of

4% of the total pitch. The standard methods of analysis may be applied to the precipitates obtained. A solution S_2 was separated from precipitate P_1. Another small quantity of water was added to solution S_2, thus precipitating a number of the less soluble constituents P_2; however, these constituents were more soluble than those constituting P_1. Known methods of analysis were applied to precipitate P_2. Another small quantity of water was added to solution S_3 which was separated from precipitate P_2. This procedure of adding water and removing the precipitate was continued until all the constituents had been extracted. The precipitates were treated to total extraction by the selective solvents: hexane, benzene, ether, chloroform, acetone. Each sub-fraction, F_1, F_2, F_3, etc. was subjected to a number of successive chromatographic treatments on alumina and silica, eventually followed by a further extraction or by a molecular sublimation. In this way, pure substances have been obtained. In this case, it was found that the main constituents are hetero-cyclic compounds with very original properties (color black with brown reflections, with a melting point greater than 360° C., insoluble in all solvents except quinoline, molecular mass greater than 3,000). In this way, there were counted about 15 substances of this type which had never previously been isolated. Among the other constituents, about 10 had more standard properties.

What we claim is:

A method of separating constituents contained in a pitch, comprising contacting the pitch with ether saturated with water to dissolve a portion of the pitch; adding an 85% alcoholic solution to the ether solution to precipitate some of the pitch constituents in the ether solution; removing the precipitated constituents from the solution thereby yielding a second solution containing the remaining dissolved constituents; chromatographing the second solution on alumina and then on silica to yield a third solution containing the remaining dissolved constituents, acetone being used as an eluant during the chromatographing steps; mixing the third solution with an aniline cyclo-hexane mixture to collect some of the constituents in the third solution in the aniline; then

chromatographing the third solution and aniline cyclo-hexane mixture on alumina to form fractions containing constituents of the pitch, and collecting the constituents in each fraction on silica by using successively as eluants: ether, cyclo-hexane, acetone, alcohol and pyridine.

References Cited in the file of this patent

UNITED STATES PATENTS

1,355,099	Weiss	Oct. 5, 1920
1,674,710	Wittek	June 26, 1928
1,868,211	Le Nobel	July 19, 1932
1,960,679	Parkhurst	May 29, 1934
2,419,011	Curtis	Apr. 15, 1947
2,549,298	Donegan	Apr. 17, 1951
2,568,159	Medcalf et al.	Sept. 18, 1951
2,730,453	Jordan et al.	Jan. 10, 1956

OTHER REFERENCES

Strain: "Chromotographic Adsorption Analysis," pages 14–28; 65–69, pub. by Interscience Publishers Inc., New York, New York (1942).

Kern: Helvitica Chimica Acta, vol. 30, 1947, pp. 1595–1599; Abst. in Chemical Abstracts, vol. 42 (1948), p. 1002i.

Wieland et al.: Liebig's Annalen der Chemie, vol. 564 (1949), pp. 199–207; Abst. in Chemical Abstracts, vol. 44 (1950), p. 1950.

Krenkler: Erdol u Kohle, vol. 2 (1949), pp. 11–16. Abst. in Chemical Abstracts, vol. 43 (1949), p. 4841e.

Zechmeister: "Progress in Chromatography 1938–1947," pages 270–272; pub. by Wiley and Sons Inc., New York, New York (1950).

Weissberger: "Technique of Organic Chemistry," vol. V ("Adsorption and Chromatography," Cassidy), pages 152–160, pub. by Interscience Publishers Inc., New York, New York (1951).

Vahrman: Fuel, vol. 30 (1951), pp. 79–82.

Green et al.: Journal of Applied Chemistry, vol. 1, No. 10, October 1951, pp. 433–437.

O'Donnell: Analytical Chemistry, vol. 23, No. 6, June 1951, pp. 894–898.

Vahrman: Journal of Applied Chemistry, Sept. 2, 1952, pp. 538–545.