UNITED STATES PATENT OFFICE.

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MERCURY SALTS OF ETHYLENEDIAMIN BASES AND PROCESS OF MAKING SAME.

SPECIFICATION forming part of Letters Patent No. 726,126, dated April 21, 1903.

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To all whom it may concern:

Be it known that we, GEORG WICHMANN and HEINRICH KIPPENBERG, chemists, subjects of the King of Prussia, residing at Berlin, Germany, have invented certain new and useful Improvements in Mercury Salts of Ethylenediamin Bases and Process of Making the Same, of which the following is a full, clear, and exact description.

This invention relates to new alkaline compounds acting as antiseptics and adapted for therapeutical purposes, especially for disinfecting the hands and the skin, which alkaline compounds consist of chemical combinations of salts of mercury with non-toxic organic bases, (as such or in the form of their carbonates,) which bases do not produce a corroding action or a coagulation of albumen.

The ethylenediamin bases are organic bases very suitable for the present purposes. Among these ethylenediamin bases, especially ethylenediamin as such, as well as in the form of its alkyl derivatives (*e. g.*, diethylethylenediamin and piperazin, which is likewise an alkyl derivative of ethylenediamin) may be used for the same purpose.

For the combination with the described organic bases according to our invention the inorganic salts of mercury and the organic salts thereof, and among the latter especially the salts of the oxids of this metal, are very suitable. These combinations are intended and adapted to be used as a substitute for the sublimate heretofore used and which is employed in the form of its solution with a strength of one to one thousand. Such sublimate solution shows in its practical use, on the one hand, the disadvantage of disagreeably exciting the skin and of causing eczema of long duration on physicians and patients and, on the other hand, the further disadvantage that it is not possible to increase without danger the strength of the said solution in order to produce a sure effect. If, however, according to the present invention, the said salts of mercury have been combined with ethylenediamin or other suitable bases, not only the disagreeable exciting action of salt of mercury on the skin is prevented or decreased down to an inconsiderable minimum, so that solutions of a greater strength can be used than is possible with sublimate alone, but also an increased action in the interior of the skin is produced in consequence of the strong alkaline or basic property of the combinations of the present invention. The combining of the said organic bases with salts of mercury shows the further advantage that now it is not necessary to employ the perchlorid of mercury, (sublimate,) which in pure solutions develops the strongest disinfecting power and simultaneously also the strongest excitement on the skin, &c., but that now it is possible to employ salts of mercury having as such a less disinfecting power and an inconsiderable exciting action and, nevertheless, to produce a better effect than by means of perchlorid of mercury alone. The following examples may illustrate the production of these combinations according to the present invention without confining ourselves to the hereinafter-described examples or exactly to the described mode of performance:

Example 1—Mercury citrate ethylenediamin.—To one hundred grams of finely-comminuted citrate of mercury which has been previously washed with alcohol and then dried on a water-bath five hundred cubic centimeters of absolute alcohol is added, the mixture is cooled with ice, and while further cooling to the same fifty cubic centimeters of ethylenediamin of ninety per cent. and one hundred and twenty cubic centimeters absolute alcohol are gradually added. By continuously stirring or shaking the whole mass the citrate dissolves fully after about twenty minutes. If small quantities of metallic mercury are liberated by chemical reaction, they may be eliminated in any suitable manner, such as by filtration or decantation. The clear and almost colorless solution is brought to crystallization by rubbing it together with a small quantity of the corresponding solid combination—*i. e.*, for example, together with a small quantity of mercury citrate ethylenediamin—whereupon from the crystallized mass the liquid adhering to the crystals is

soaked off and then the crystals are washed with a mixture of alcohol and ether and then with ether and dried, preferably by the aid of a vacuum. The thus-obtained mercury citrate ethylenediamin forms white needles very readily soluble in water. The solution shows a strong basic or alkaline reaction. The combination contains 43.1 per cent. mercury and begins at about 110° centigrade to sinter or to frit. The combination shows a development of gas at 137° centigrade and becomes gray. By a continued heating on the water-bath metallic mercury is liberated. In order to produce a disinfecting liquid containing the desired combination, it is generally to be preferred, although not necessary, to isolate such combination. In this case the latter may be produced in solution, and this solution may be employed in a suitable dilution as disinfectant. Such solution may be obtained, according to this example, by pouring two liters of water on about one kilogram of citrate of mercury and adding thereto during heating about four hundred grams of ethylenediamin and then diluting the resulting liquid by means of about six to seven liters of water.

Example 2—Mercury sulfate ethylenediamin.—To a mixture of one hundred grams of sulfate of mercury with fifty cubic centimeters of water sixty grams of ethylenediamin of ninety per cent. dissolved or distributed in one hundred cubic centimeters of water are gradually added with cooling and agitation, and to the clear solution obtained after this operation about one and one-half liters of ninety-six per cent. alcohol are added, whereby an oily precipitate is formed which soon becomes solid. The liquid adhering to this precipitate will then be soaked off, and the precipitate is thereafter washed with alcohol and forms the desired combination.

The mercury sulfate ethylenediamin forms white needles readily soluble in water and difficultly soluble in alcohol. At a temperature of about 180° centigrade the compound becomes brown, and at about 210° centigrade a full decomposition of the said needles sets in, but without melting or foaming up or effervescing.

By means of other salts of mercury analogous combinations can be obtained in a similar manner. Examples of such combination may be described as follows:

Mercury cyanid ethylenediamin forms white needles readily soluble in water and difficultly soluble in alcohol. At a temperature of about 144° to 145° centigrade it melts after preceding fritting or the like with slight formation of bubbles, thereby forming a clear liquid.

Mercury acetate ethylenediamin forms at the evaporation of the alcoholic solution colorless crystals very easily soluble in water as well as in alcohol.

Mercury benzoate ethylenediamin forms white glossy small leaves readily soluble in water, in some degree more difficultly soluble in alcohol, and melting at about 107° to 108° centigrade without becoming dark.

Mercury nitrate ethylenediamin forms white crystals readily soluble in water, but not so readily soluble in alcohol.

In employing alkyl derivatives of the ethylenediamin analogous compounds are obtained.

Examples: Mercury nitrate diethylethylenediamin—Thirty-two grams of mercury nitrate are introduced into a solution of thirty-six cubic centimeters of diethylethylenediamin of sixty-six per cent. (obtained by the action of two molecules of ethylenebromid on alcoholic solutions of strong ethylenediamin) in sixty-four cubic centimeters of absolute alcohol. The mixture is heated. The resulting reddish precipitation is filtered and the clear solution is evaporated in a vacuum. The residue of this evaporation consists of dull crystals, which become white by repeated dissolving in absolute alcohol and precipitating with ether. This product is readily soluble in water, is slightly hygroscopic, and melts at 148° to 151° centigrade with decomposition.

Mercury sulfate diethylethylenediamin.—Thirty grams of mercury sulfate are introduced into a solution of seventy-two cubic centimeters of diethylethylenediamin of sixty-six per cent. in fifty cubic centimeters of absolute alcohol. The mixture is heated, and there results in the course of time a complete solution. The solution obtained is evaporated in a vacuum over sulfuric acid. The product is readily soluble in water and melts at 124° to 125° centigrade with decomposition.

Mercury perchlorid-diethylethylenediamin melts at 159° to 160° centigrade, is difficultly soluble in cold water, more readily soluble in hot water.

Mercury cyanid diethylethylenediamin melts at 108° to 110° centigrade and is soluble in hot water.

Mercury succinate diethylethylenediamin is readily soluble in water and melts at 128° to 130° centigrade with complete decomposition.

Mercury salicylate diethylethylenediamin melts at 181° to 183° centigrade and is soluble in water.

Mercury acetate piperazin.—In obtaining this product it may be manipulated as follows: Sixteen grams of mercury acetate, very finely powdered, are mixed with one hundred cubic centimeters of absolute alcohol. There- to ten grams of piperazin free of water and dissolved in one hundred and fifty cubic centimeters of alcohol are added and well mixed. The mass is then slightly heated and allowed to stand about twenty hours. Then the product obtained is drawn off, washed with alcohol-ether and ether, and then dried. The product thus obtained is readily soluble in water, becomes black when heated in a cap-

illary tube, and melts at 188° centigrade with complete decomposition at 198° centigrade. Boiled with alcohol this compound is not altered as the mercury acetate.

It is not necessary to employ the mentioned organic bases as such, for they may be used in the form of their carbonates, which in this case are brought together with the said salts of mercury in quantities calculated according to the molecular relations. If the combination is dissolved in water or if to a solution of the carbonate of ethylenediamin or of a carbonate of an alkyl derivative of the ethylenediamin a salt of mercury is added with evolution of carbonic-acid gas, a solution of the same product is formed as results from the use of the said organic bases as such—that is, in their free state. In some cases it is suitable to produce the solution in this manner—as, for example, if combinations are in view which are hygroscopic, and consequently not fully precipitable by alcohol. This may be illustrated by the following example:

Mercury citrate ethylenediamin carbonate from ethylenediamin carbonate may be obtained as follows: To a solution of 0.67 grams of carbonate of ethylenediamin in 8.6 grams of water one gram of citrate of mercury is slowly and gradually added. A solution takes place with evolution of carbonic-acid gas. In order to obtain the product in a solid state, either the solution may be evaporated *in vacuo* until dryness or the product may be precipitated from the concentrated solution by the addition of suitable precipitants—such as alcohol.

Mercury citrate piperazin carbonate.—One gram of citrate of mercury is added to a solution of about two grams of piperazin carbonate in water. A solution takes place with escape of carbonic acid. The product in a solid state is obtained as just before described. From the combinations in a solid form it is preferred to form tablets, lozenges, or the like.

Our invention does not relate, broadly, to antiseptic compounds of mercury; but only to alkaline antiseptic compounds of mercury and the mode of producing such compounds.

Since for the carrying out of the present invention the indicated organic bases may be employed as such or in the form of their carbonates, the latter are fully equivalent to the said bases as such, and therefore in this specification by "organic bases" are to be understood not only the bases as such, but also their carbonates.

We claim as our invention—

1. New disinfecting products, consisting of combinations of salts of mercury with ethylenediamin bases, which combinations have an alkaline reaction and are soluble in water and do not corrode the skin and are adapted to be used as a substitute for the sublimate.

2. The herein-described process which consists in reacting on mercury salts with ethylenediamin bases, then separating the combination by evaporating the liquid and mechanically removing the liquid adhering to the solid product and by washing, substantially as and for the purpose set forth.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

GEORG WICHMANN.
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Witnesses:
JOHANNES D. HEIN,
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