UNITED STATES PATENT OFFICE.

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SLOVENT FOR PYROXYLIN, &c., AND PROCESS FOR MAKING THE SAME.

972,953. Specification of Letters Patent. **Patented Oct. 18, 1910.**

No Drawing. Application filed January 21, 1909. Serial No. 473,499.

To all whom it may concern:

Be it known that I, HENRY V. WALKER, a citizen of the United States, and resident of Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in Solvents for Pyroxylin, &c., and Processes for Making Same, of which the following is a specification.

The preferred method of practicing my present process and of obtaining the novel solvents of my present invention is related to my process for making hypochlorous acid, the subject of my application, simultaneous herewith, for United States Letters Patent Serial No. 473,498, and is also related to my process for making chlorhydrins, the subject of my application, simultaneous herewith, for United States Letters Patent Serial No. 473,497.

As examples of the new solvents within my present invention, I have specifically named gas-naphtha olefin oxids, and will now proceed to describe their method of preparation and the characteristics of the solvents themselves.

My preferred starting material is so-called gas-naphtha, a by-product of the ordinary commercial treatment of petroleum. Thus, in the process of refining crude petroleum, the oil is subjected to distillation, the lighter products, such as naphtha and benzin, coming over first. These are followed by the burning oil fraction. At a certain stage of this period of the distillation, it is found that the product coming over is of much lower boiling point, gravity and flashing point than that preceding it. This peculiarity is attributed to a cracking up of the higher hydrocarbons under the influence of the high temperature prevailing in the distillation. It is usual to run the distillation until the product has again risen in gravity, etc., to that of the initial burning oil fraction. This secondary product which is collected separately is then redistilled, yielding a distillate called "gas-naphtha" and a residue which is added to the burning oil fraction. This material known in the refineries as gas-naphtha has been so called from the use to which it has heretofore been put, namely, the manufacture of gas for heating purposes and the enrichment of illuminating gas. Whereas American petroleum consists almost exclusively of saturated hydrocarbons or paraffins, the gas-naphtha contains about 40% of olefins and about 60% only of paraffins. Its boiling point ranges from 35° to 125° centigrade. It is believed that its olefins range from 5 to 8 carbons and that they are primary in structure. For example, the C_6 olefin may be represented by the formula:

$$CH_3—CH_2—CH_2—CH_2—CH=CH_2.$$

As part of the process, I convert the olefins of this gas naphtha into chlorhydrins. It might be thought that such a mixture of olefins and paraffins as is contained in this gas-naphtha would react with hypochlorous acid produced in any of the usual ways to form chlorhydrins (although so far as known to me no chlorhydrin or oxid of a primary olefin having five or more carbons has been so produced) but it was found not to be so. There are two described methods of preparing hypochlorous acid. The first of these depends essentially upon the reaction of chlorin with mercuric oxid. This method is too expensive to be thought of on account of the great cost of the mercuric oxid employed. The second of these comprises the treatment of hypochlorites of sodium, or calcium, with a dilute acid. In each case free chlorin was present, the yield of hypochlorous acid was small and its solution was dilute. Both of these methods, therefore, were unavailable. I was, therefore, obliged to find another method of producing the hypochlorous acid. I discovered that if there was added to a solution of a suitable hypochlorite, for instance, hypochlorite of soda, a sufficient quantity of a suitable bicarbonate, for instance, bicarbonate of soda, to convert both the free alkali and the sodium in combination in the hypochlorite, into sodium carbonate, then a solution was obtained which contained hypochlorous acid, free from chlorin and which reacted readily with the olefins of the gas-naphtha.

I utilize this new process of making hypo-

chlorous acid to make the aforesaid chlorhydrins from the gas-naphtha olefins as follows: Thus, the gas-naphtha, comprising a mixture of olefins and paraffins as stated or other suitable material containing the olefins, is first placed in a vessel provided with means for agitating and cooling its contents. In another suitable vessel is placed a solution in water of a suitable hypochlorite, for instance, hypochlorite of soda, dissolved in water. It is preferable to use a separate vessel as stated, but not at all essential, since the gas-naphtha, hypochlorite and bicarbonate of soda or the equivalent materials may be all three mixed together and allowed to react in the same vessel. A solution of the hypochlorite containing from 15 to 25 per cent. of NaOCl is of convenient strength. To this is added a sufficient quantity of a soluble bicarbonate of a fixed alkali, preferably bicarbonate of soda, to react therewith to form hypochlorous acid. A proper proportion to employ is about 75 parts of the hypochlorite of soda (NaOCl) to about 85 parts of the bicarbonate of soda ($NaHCO_3$). The bicarbonate may be added in the form of a saturated aqueous solution, or mixed with an amount of water insufficient for solution or in the dry state. There is no free chlorin produced. The mixture of hypochlorite and bicarbonate of soda in which the hypochlorous acid formed is then added to the vessel containing the gas naphtha, or other material, and the contents are agitated and cooled. The reaction will take place at ordinary temperatures without cooling, but the best results are obtained by preventing the rise of temperature due to the reaction and maintaining the temperature at or below 15° centigrade. This reaction should continue for about four hours. At the end of that time the oily portion of the liquid containing the chlorhydrins is allowed to separate from the aqueous portion of the liquid, the latter being drawn off and rejected. The oily portion is then washed with a small amount of water to remove any hypochlorite which might remain and it is dehydrated. If it is desired to accomplish such dehydration quickly, calcium chlorid may be employed. If time is not essential, the water may be allowed to separate out by gravity. The discovery upon which this part of the process depends is that the chlorhydrins remain in the oily part of the liquid and not in its aqueous part. The paraffins, or residual hydrocarbons, which are mixed with the chlorhydrins are then removed. This is accomplished by distillation at a suitable temperature below the boiling point of the chlorhydrins, which is about 170° centigrade. Such a temperature is about 140° centigrade. Of course, the temperature during this step of the process must be lower than that at which the chlorhydrins will be carried over. After such distillation, the residual liquid consists of the chlorhydrins sought to be obtained.

The reactions apparently involved may be illustrated in connection with the C_6 olefin:—

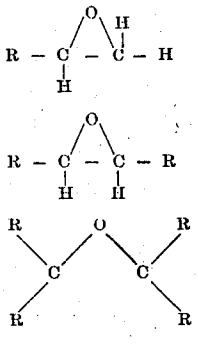
(1) $NaOCl + NaHCO_3 = Na_2CO_3 + HOCl$

(2) $C_6H_{12} + HOCl = C_6H_{12}.OH.Cl$
(Chlorhydrin of the C_6 olefin.)

In carrying out the above part of the process, it is advisable first to ascertain the percentage of olefins in the material employed by determining the amount of bromin absorbed, using the well known methods for this purpose. From this, the quantity of hypochlorous acid necessary to be used is shown by the above equation No. 2, a slight excess of such acid being used to insure as complete a conversion of the olefins as possible. The next step in the process is to treat the residual chlorhydrins produced as above with a suitable caustic alkali. For this purpose, I use the caustic alkalies, slaked lime, caustic potash or soda, preferring lime. In practice, to 1,000 grams of the chlorhydrins, I add a mixture of about 350 grams of lime mixed with about 1 liter of water. This chlorhydrin-lime mixture is heated to boiling in a suitable vessel with a return condenser for about one hour; it is then distilled with steam until no more oil passes over. This oil is separated from the water and agitated while cold with a 50% solution of caustic soda for the purpose of removing a small portion of impurities which may be present. It is then separated and is dehydrated with carbonate potash or calcium chlorid and distilled when it passes over as a water-white fluid. The described distillate is a mixture of olefin oxids. If desired, it may be separated by fractional distillation into separate parts but this is a mere matter of expediency depending upon the particular use in view. These olefin oxids either separately or as a mixture constitute a novel solvent for pyroxylin and other substances.

The gas naphtha, which is my preferred material for the production of the chlorhydrins, is a mixture of olefins and paraffins ranging from C_5H_{10} and C_7H_{12} to C_8H_{16} and C_8H_{18}. Its boiling point ranges from 30° C. to 125° C. By conversion into chlordydrins and decomposition with caustic alkali the olefins therein are converted into olefin oxids, from $C_5H_{10}O$ to $C_8H_{16}O$. The olefin oxids of five or more carbon atoms, heretofore produced have been of secondary or tertiary structure, whereas the olefins contained in the gas naphtha are of normal or primary structure. The oxids derived therefrom are therefore new bodies. These dif-

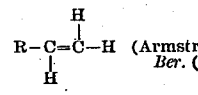
ferences in structure may be illustrated as follows, R representing any alkyl radical:



The facts upon which it is claimed that the new olefin oxids made from gas-naphtha have the primary structure are as follows:

1. The paraffins of American petroleum are of primary structure.

2. The olefins produced by the action of heat on the paraffins are also of primary structure,



(Armstrong and Miller, *Chem. Soc.* 1886 I, 79-93. *Ber.* (Ref.) 19,244.)

3. The olefin oxids prepared by me do not combine with water. This is a characteristic property of primary olefin oxids as distinguished from the secondary or tertiary oxids, which do combine with water to form glycols.

I am aware that Wurtz (A. ch. (4) 4, 184) has described the preparation of a hexylenoxid, an olefin oxid at one time thought to possess the primary structure, and which was prepared from the hexylen derived from mannite, but subsequent investigations have shown its structure to be secondary. (Henry *Compt. Rend.* 97,260.) The olefin oxids produced by me, therefore, are the first of the primary structure which have been made.

In some instances instead of separating the chlorhydrins from the paraffins as described, I may proceed as follows: After reacting on the gas naphtha with the hypochlorous acid mixture and separating the oily from the aqueous portion, I may distil the entire oily layer directly with caustic alkali, without separating the paraffins. The oily portion of the resulting distillate, after separation and dehydration in the usual manner, constitutes a novel solvent for various varnish gums, and when the percentage of olefins in the primary material is sufficiently high, for pyroxylin.

The mixture of olefin oxids produced as above described, and which constitutes a novel solvent for pyroxylin possesses several important advantages. By its use pyroxylin may be obtained in strong transparent films, properties heretofore commercially obtainable only by the use of amyl acetate as a solvent. My novel solvent is produced from petroleum, a domestic product available in unlimited quantities, as contrasted with amyl acetate, produced from fusel oil, mainly an imported product, of which the supply is necessarily limited. By the use of my novel solvent, pyroxylin may be employed for many indicated purposes for which it hitherto could not be used, because of the high cost of amyl acetate. My novel solvent may also be employed not only as a solvent for pyroxylin, but for other substances such as rubber, asphalt, sundry varnish gums such as copal, kauri and the like, and oils such as boiled linseed-oil. The new solvent may also be diluted with a number of other liquids such as benzin and similar petroleum products which while not themselves solvents for the materials dissolved by the new solvent, nevertheless are miscible to a considerable extent with said solvent without annulling its solvent properties. For instance, if the new solvent is employed for dissolving pyroxylin it may be diluted with benzin even up to 30% in which dilution it will still dissolve pyroxylin although benzin itself does not dissolve this substance.

The olefin oxids derived from "gas naphtha" have a slight ethereal odor, are insoluble in water, and range in specific gravity from about 0.830 to about 0.855 and in boiling points from about 70° to about 145° C. according to their carbon content. They are colorless and readily miscible with the usual organic solvents, ether, alcohol, acetone, benzin, benzol, carbon tetrachlorid, and combine with hydrochloric acid with formation of the corresponding chlorhydrins.

What I claim as new and desire to secure by Letters Patent is:

1. The process of preparing a novel solvent which consists in mixing a bi-carbonate of a fixed alkali and a solution containing a hypochlorite of a fixed alkali, causing the mixture to react with gas naphtha, separating the oily from the aqueous portion of the reaction product, and distilling the oily portion with a caustic alkali.

2. The process of preparing a novel solvent which consists in mixing a bi-carbonate of a fixed alkali and a solution containing a hypochlorite of a fixed alkali, causing the mixture to react with gas naphtha, separating the oily from the aqueous portion of the reaction product, and distilling the oily portion with slaked lime.

3. As a new product of manufacture, an oxid of a primary olefin having approximately from five to eight carbon atoms, both inclusive.

4. As a new product of manufacture, an oxid of a primary olefin obtained from gas

naphtha, having approximately from five to eight carbon atoms, both inclusive.

5. As a new product of manufacture, a mixture of a primary olefin oxid having approximately from five to eight carbon atoms, both inclusive, and a diluent, such as benzin, which mixture is capable of dissolving pyroxylin.

6. As a new product of manufacture, a mixture of an oxid of a primary olefin obtained from gas naphtha, and having approximately from five to eight carbon atoms, both inclusive and a diluent.

7. As new products of manufacture, the olefin oxids, derived from gas naphtha having a slight ethereal odor, insoluble in water, ranging in specific gravity from about 0.830 to about 0.855, and in boiling points from about 70° C. to about 145° C. according to their carbon content, being colorless and readily miscible with the usual organic solvents, ether, alcohol, acetone, benzin, benzol, carbon tetrachlorid, and having as a distinguishing chemical property that of combining with hydrochloric acid, with formation of the corresponding chlorhydrins.

Witness my hand this 19th day of January 1909, at New York, N. Y.

HENRY V. WALKER.

Witnesses:

WILLIAM R. BAIRD,

STEPHEN S. NEWTON.