This application is a continuation-in-part of my co-pending applications Serial No. 818,501 filed June 3, 1959, and Serial No. 862,482 filed December 29, 1959, both of said applications being incorporated herewith by reference.

This invention relates to ion flotation method, and more particularly to a process for the recovery of organic ions and inorganic ions from solution by contacting the ions with an ionic organic reagent to form an insoluble reaction product, which adheres to a gas-water interface and is thereby buoyed to the surface by bubbling, and thereafter separating the insoluble reaction product from the solution.

In ion flotation procedures in which insolubilized ions are contacted with air bubbles to buoy or lift the insolubilized ions to the surface, care must be exercised in order to avoid the formation of supernatant froth on the surface as well as the creation of turbid colloids near the surface. Both of these phenomena are liable to result in inefficiency in the recovery of the desired ions.

An object of the present invention is to provide a process in which frothing and the creation of turbid colloids are substantially avoided. A still further object is to provide an easy process in which the desired product, as it rises with the air bubbles, is collected within a liquid layer which may be withdrawn for the recovery of the process. A still further object is to provide in an ion flotation process of the character described a liquid layer supported on the solution body, the liquid layer being immiscible with the body and serving to catch and retain the product as it is buoyed upwardly by the bubbles. Yet another object is to provide a process in which an aqueous solution of the desired product is surmounted by a non-aqueous layer by which the product is washable, which layer takes up the product as it is raised in the flotation operation, the process being continuous in that the non-aqueous layer may be continuously withdrawn and the solution continuously fed during the separating operation. Other specific objects and advantages will appear as the specification proceeds.

In the separating operations described in my co-pending applications Serial No. 818,501 and Serial No. 862,482, ions are recovered from solution in the substantial absence of undissolved mineral particles recoverable by usual flotation procedures by contacting the same in aqueous solution with a collector ion of opposite charge to the ion to be recovered. A liquid layer, immiscible with water, above the solution, and thus catch the product as it rises up with the bubbles. If the bubbling rate is kept relatively slow, no froth at all is produced and the desired product is captured by the layer before colloids are formed.

By way of example, a layer of octyl alcohol was placed over the solution body for the recovery of separated pyrithione ionomers. No froth at all was produced, and the insoluble reaction product was recovered entirely in the layer of octyl alcohol. The process was carried on continuously in a tank holding the aqueous solution and the supernatant non-aqueous layer, bubbles being introduced at a slow rate into the lower port of the tank and the supernatant non-aqueous layer being drawn off continuously. The octyl alcohol is a solvent having polar characteristics adapting it very well for collection of products such as are produced by the contacting of ions with amphiphilic substances of opposite charge.

The collectors utilized in the process of my invention are, generally speaking, the ionic surface-active collector which are utilized in ore flotation procedures. These collectors must have at least one hydrophilic center of activity and at least one aerophilic center of activity. They must have an electrical charge which is opposite to the ion which it is desired to collect if the process is to be operative.

A surface-active anionic collector, i.e., a collector yielding, in aqueous solution, a surface-active ion bearing a negative charge, for example, a lauric acid soap, is used to remove a soluble cation from solution. Conversely, a surface-active cationic collector, i.e., a collector yielding, in aqueous solution, a surface-active ion bearing a positive charge, for example, lauryl pyridinium chloride, is used when it is desired to remove a desired anion from solution.

Cationic collectors used in my novel process, for the most part, are compounds having one or more amine nitrogens. These compounds include primary, secondary and tertiary fatty alkyl, aryl and diarylamines, and their salts and the corresponding fatty amine or ammonium salts. The amines include the picolines, pyridines, quinolines, and their homologs and lower alkyl substituted analogs.

Examples of cationic collectors which will react with organic anions in polar solutions include the quaternary ammonium compounds, such as trimethyl-n-octylammonium chloride, trimethyl-n-decylammonium chloride, trimethyl-n-dodecylammonium chloride, trimethyl-n-octadecylammonium bromide, triethyl-n-hexadecylammonium iodide; mixtures of quaternary salts derived from tallow fatty acids, from cottonseed oil fatty acids, from soybean oil fatty acids and coconut oil fatty acids, from mixtures of fatty acids derived from tallow, corn oil, soybean oil, coconut oil; alkyl amines such as diamylamine, didodecylamine, n-decylamine, n-tetradecylamine, tri-n-octadecylamine, n-octadecylamine and mixtures of amines; and miscellaneous collectors such as ammonium phenyl - nitrosophenylxylamine, 1 - n-dodecylpyridinium iodide, octadecyl β-hydroxyethyl morpholinium bromide, β-stearamidophenyl trimethylammonium methylsulfate, octadecyl pyridinium iodide, octadecyl α-picolinium bromide, hexadecyl quinolinium bromide, decylbutylpyridinium chloride, dodecyldiphenyldimethylammonium phenylsulfonate, dimethylbisdodecylammonium phenylsulfonate, 2 - mercaptobenzothioazole derivatives, various imidazoline and imidazolidine derivatives, and dimethyl-n-hexadecylbenzylammonium chloride.

Anionic collectors are of two types: the oxhydroly compound, where a metal or hydrogen is connected to the hydrocarbon element of the collector through an oxygen atom, and the sulfhydryl type where the connection is made through a sulfur atom. The oxhydroly collectors include carboxylates, acid alkylsulfates, sulfonates and phosphates and phosphonates. The sulfhydryl compounds include mercapto, thiacarboxylics (xanthates), thioureas and dithiophosphates. Examples of anionic collectors include the acids and sodium, potassium or ammonium salts of rosin, the tall oils and animal and vegetable oils; naphthenic acids; sodium- n-octylsulfate; potassium- n-dodecylsulfate; the ammonium salt of n-dodecylthiodyleneglycol sulfate; the sodium salt of crude or refined petroleum...
sulfonic acid; \( \beta \)-phenylpropionic acid; pelargonic acid; mixtures of acids derived from linseed oil, soybean oil, palm oil, corn oil and cottonseed oil; monosodium \( \alpha \)-sulfopelmatate; disodium \( \alpha \)-sulfostearate, 1,3-diphenyl-2-thio-
urea and thiocarbanilide. The above-described examples of cationic anionic collectors are but a few of the many collectors which are known to be commercially practicable and which are used in flotation procedures.

The number of carbon atoms in the aerophilic portion or portions of the collector molecule required to impart desired aerophilic properties to the collector varies with the type of collector. Generally from 5 to about 24 and preferably from 8 to 22 carbon atoms are required in at least one aerophilic portion of the collector molecule. My preferred cationic and anionic collectors are derived from plant and animal triglycerides, preferably vegetable or marine animal triglycerides. These glycerides can be hydrolyzed to free their fatty acids which can then be utilized as anionic collectors per se, or which can be converted to ammonium or alkali metal salts for similar purposes. When a cationic collector is desired, the fatty acids are converted to amines, nitriles or quaternary salts by known means. It is also preferred that the hydrocarbon chains of these collectors contain carbon to carbon unsaturation. Where quaternary ammonium collectors, diamine collectors or triamine collectors are utilized, it is especially preferred that the collectors contain at least 1 hydrocarbon radical containing from 8 to 22 carbon atoms.

The term “insoluble reaction products” and similar terms are used throughout this specification. The term insoluble does not mean that the “solubility” is an equilibrium between the ions in solution and a solid ionic crystal, rather it is intended that the term encompass instances wherein the reaction product is composed of oppositely charged ions which are not independent as they have lost some entropy. Thus, the term applies to products (other than soluble reaction products) adsorbed at the solvent-bubble interface, i.e., the unitary product molecules are no longer randomly dispersed throughout the solution but are, in a major proportion, localized at the solvent-bubble interface. The products at the interface may be thought of as crystals containing only one molecule of product. As these crystals are forced closer together in the draining froth, they form a scum which is highly insoluble rather than larger crystals.

The range of amounts of collector required to collect a given amount of ion is great. I prefer to utilize an amount of collector ranging from about 0.001 to 10 equivalents of collector/equivalent of ion. A still more preferable range of equivalents is 0.1–10 equivalents of collector/equivalent of ion. Still more preferable is the utilization of stoichiometrically equivalent amounts of collector/equivalent of ion to be collected.

The reaction products formed when the above-identified collectors are contacted are removed from solution by flotation, i.e., are removed from solution by means of substantially nonreactive gaseous bubbles. Useful bubble materials include gaseous hydrocarbons such as methane, ethane and butane; gaseous halogenated hydrocarbons such as the Freons; and gases such as air, carbon dioxide, nitrogen and argon. I prefer to utilize air to remove insoluble reaction products from the solvents used in the ion recovery process of my invention.

The liquid collection layer should be immiscible with the liquid from which the ions are being recovered and should have some polar characteristics adapting it for collection of the desired ions. For example, octyl alcohol is useful, because it has sufficient polar characteristic to dissolve the flotation product but is not so polar that it itself is soluble in water. It is not necessary that the supernatant layer be a solvent; it is sufficient that the reaction product be wettable by the layer or phase. In other words, the reaction product is taken up or held by the liquid collection layer either by way of solution or by wetting. Other examples of suitable solvents or wetting agents are: benzene, mixtures of benzene octyl alcohol, mixtures of petroleum and higher alcohols.

Other characteristics of the liquid collection layer are that it must be insoluble or only very slightly soluble in water, it must be lighter than water or solutions of salts in water, it should not react chemically with the water or with the flotation product.

By utilizing the collection layer of liquid, immiscible with the liquid from which the ions are recovered, it is found that the reaction product is taken up into the layer, while any entrained liquid carried to the surface drops back into the solution as small droplets. Frothing or the formation of turbid colloids are minimized and may be entirely eliminated.

Specific examples of the process which may be set out as illustrative of the process are as follows:

**Example I**

3 mg of methyl orange was dissolved in 300 ml of water, buffered to pH 6.5 with sodium bicarbonate and placed in a No. 4 sintered glass Büchner funnel, diameter 3". 25 ml of isooctyl alcohol was placed on the surface of the solution. 3 mg of dodecyl trimethyl ammonium chloride was dissolved in 0.5 ml of absolute alcohol, heated to boiling for a few seconds and added to the solution by means of a capillary tube that passed through the octyl alcohol layer and reached almost to the sintered glass plate. Nitrogen gas was sparged through the sintered glass, thus generating very small bubbles. The bubble rate was carefully adjusted so as to disturb the octyl alcohol layer as little as possible. This resulted in the small bubbles accumulating under the octyl alcohol and gradually coalescing to form larger bubbles which rose through the octyl alcohol. As they did so, the product formed between the methyl orange anion, and the quaternary ammonium cation, was stripped from the bubble and dissolved in the octyl alcohol. From time to time the entrained water carried to the surface dropped back as small droplets. After 15 minutes, the aqueous layer was completely decolorized and the octyl alcohol layer was bright yellow, showing that the methyl orange anion had been removed from the water and dissolved in the non-aqueous solvent.

**Example II**

3 mg of Lauth's violet, a cationic dye, was dissolved in 300 ml of water, made slightly acidic with hydrochloric acid and placed in a similar vessel as above, with 25 ml of isooctyl alcohol placed on the surface. 3 mg of \( \alpha \)-sulphonic acid was dissolved in 3 ml of absolute alcohol, heated to boiling for a few seconds and added to the solution as in the previous example. The same procedure was carried out. After 15 minutes, the aqueous solution, which had been violet, was completely decolorized, and the color had gone into the octyl alcohol, showing that the cation dye had combined with the sulphonate anion and been collected by the octyl alcohol.

**Example III**

0.01 g each of cobalt and nickel chlorides were dissolved in 300 ml water and just enough ammonia was added to redissolve the hydroxides formed. The solution was placed in a similar vessel to that in Example I and 25 ml of isooctyl alcohol was placed on the surface. 6 mg of lauric acid was dissolved in 10 ml of alcohol and 3 mg KOH added to convert to potassium laurate and taken to boiling. This solution was added, under the octyl alcohol, 2 ml at a time with bubbling as before. After each addition, bubbling was continued for 5 minutes and the contents of the funnel was removed to a separatory funnel, and the octyl alcohol layer was separated. The solution was then put back in the Buchner funnel and fresh octyl alcohol added, and the next 2 ml of collector added. After the first addition, the octyl alcohol was greenish, there being some undissolved
product in it. The octyl alcohol contained cobalt but only a trace of nickel. The fifth and final sample of octyl alcohol, which was blue green, contained only nickel. This illustrates that the selectivity shown by ion flotation applies also if flotation is into a non-miscible solvent. It also illustrates that the product, brought up by the bubble, does not necessarily need to be soluble in the non-aqueous phase, but that it is sufficient if it is wettable by the non-aqueous phase.

**Example IV**

300 ml. of a saturated solution of cupric chloride was placed in a Büchner funnel as before and 25 ml. of isooctyl alcohol placed on the surface. 50 mg. of laurylamine was dissolved in 5 ml. of absolute alcohol, just acidified with HCl and heated to boiling and added to the solution of cupric chloride. Air was bubbled for 10 minutes, by which time the octyl alcohol had become bright yellow. On separating this layer, the yellow color was proved to be due to the CuCl₂ ion, so that the experiment shows the presence of this ion in a saturated solution of cupric chloride, and that it is collected by laurylamine, the laurylaminium cupric tetrachloride being soluble in octyl alcohol.

**Example V**

4 mg. of potassium ferrocyanide tribhydrate was dissolved in 200 ml. of water and the solution adjusted with potassium hydroxide to pH 10.5. It was placed in a No. 4 sintered glass Büchner funnel, 2" diameter, and 10 ml. of iso-octyl alcohol was placed on the surface. 10.8 mg. of lauryl pyridinium chloride, an amount exactly equivalent to the ferrocyanide ion was dissolved in petrol ether (60-80° C.) and carefully taken to dryness. It was then dissolved in 5 ml. of absolute alcohol, taken to boiling and added to the ferrocyanide solution under the octyl alcohol. Air was bubbled through slowly for 30 minutes, the octyl alcohol layer was carefully separated, the octyl alcohol carefully evaporated off, and the residue destroyed with concentrated sulphuric acid and then ignited with potassium pyrosulphate. The iron was determined colorimetrically as ferric thiocynate and showed that 97.5% of the ferrocyanide ion had been collected in the octyl alcohol layer.

**Example VI**

0.3 g. of copper sulphate was dissolved in 250 ml. of water. Ammonia was added until the hydroxide just redissolved. The solution was added to a Büchner funnel as in Example I. 30 ml. of benzene and 10 ml. of butyl alcohol was mixed and placed above the surface of the solution. 0.2 g. of lauric acid was dissolved in 10 ml. of alcohol and converted to the laureate by adding potassium hydroxide. This was added in two stages at 10 minute intervals, through a capillary below the surface of the non-aqueous layer. Air was bubbled through slowly for 20 minutes. At the end of that time, the upper layer was a deep blue showing that most of the copper had concentrated in it, but there was still a pale blue color in the aqueous solution. This is attributed to the fact that butyl alcohol is slightly soluble in water and takes some of the copper laureate with it. The copper laureate, dissolved in the benzene-butyl alcohol mixture, was easily extracted by shaking with dilute HCl.

The new process provides a number of advantages in the flotation separation of ions. In comparison with solvent extraction, the process is versatile in that it separates the collector and the solvent stages. Whereas in solvent extraction, the quantity of solvent is related to the quantity of aqueous solution, in the present process the quantity is related to the amount of ion extracted, the upper limit being imposed by the solubility of the ion-soap compound in the solvent. By regulating the height of the solvent bed or layer, it is possible to prevent entrained water drops rising to the top of it. Furthermore, loss of solvent, which is always a bugbear in solvent extraction, is minimized.

There is the further advantage in that the danger of emulsification is minimized. In solvent extraction, the rate of extraction is determined by the rate of diffusion into the solvent droplets, whereas here the adsorption is on the surface of the bubbles, and desorption into the solvent is off the surface of the bubbles, so that the rate is controlled by the bubble rate.

Further, in comparison with solvent extraction, it is pointed out that the selectivity, which is one of the main values of ion flotation, is well retained by the present process, the operation combining, in effect, the advantages of ion-exchange with solvent extraction or wetting.

Finally, the present process lends itself to continuous processing. Reclaiming the ion and the solvent may be accomplished through any of the well-known methods, as, for example, by distilling the solvent to produce a residue of the same soap compound that would have been collected in the scum in ion flotation.

While, in the foregoing specification, I have set forth illustrative examples and procedures in considerable detail for the purpose of setting out embodiments of the invention, it will be understood that such details of procedure may be varied widely by those skilled in the art without departing from the spirit of my invention.

I claim:

A process for the recovery of ions from an aqueous solution thereof comprising adding to the solution collector ions having an electrical charge opposite to that of the ions to be recovered to form an insoluble reaction product of said ions in said solution, disposing upon the surface of the solution a floating layer of a non-aqueous liquid immiscible with said solution and having polar characteristics adapting it for collecting said reaction product, introducing gas into the solution having the floating liquid layer disposed thereover in the form of small bubbles at a rate which leaves the floating liquid layer substantially undisturbed to buoy the reaction product to the surface of the solution and into the floating liquid layer where it is collected.

**References Cited by the Examiner**

**UNITED STATES PATENTS**

1,619,036 3/1927 Ravnestad 210-44
2,757,081 7/1956 Hure et al. 23-312
2,869,979 1/1959 Grinstead 23-14.5
2,933,569 9/1960 Last et al. 210-44
3,054,747 9/1962 Gadak et al. 210-44

**OTHER REFERENCES**


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