

Alkaline Persulfate as an Analytical Reagent

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Though persulfate in acid¹ or neutral solutions² has frequently been applied as a qualitative reagent, its use in alkaline³ solution has been limited to the precipitation of cobaltic oxide. Using potassium persulfate in potassium hydroxide solution, instead of ammonium persulfate in sodium hydroxide solution as used by Pozzi-Escot, a more complete precipitation of Co_2O_3 can be made (1:1,000,000).

Comparable precipitations of black Ni_2O_3 can be made from nickelous solutions by treatment with alkaline persulfate. In the absence of cobalt, it is a characteristic test for nickel, since its black will cover up the colors of other metallic hydroxides. Also in the presence of metals whose hydroxides are soluble in fixed alkalies, it can give a separation of either nickel or cobalt or both of these metals. Conversely nickel or cobalt is a qualitative test for persulfate.

Cyanides.—Alkaline persulfate oxidized cyanides, ferricyanides, ferrocyanides, nitroprussides and thioazates to cyanic acid, as indicated by the following test. To any one of these, add the reagent and heat to boiling. Acidify with hydrochloric acid and again make alkaline. Moist red litmus paper on the convex side of a watch glass covering the beaker turns blue, owing to the liberation of ammonia. Without persulfate, the litmus paper remains unaffected.

Thiosulfate, but not sulfite, or arsenite, is oxidized by the reagent. Sodium peroxide liberates oxygen. These and other reactions will be studied.

¹ Caro, *Z. angew. Chem.*, 845 (1898); Marshall, *Chem. News*, 83, 76 (1901).

² Merk, *Pharm.-Ztg.*, 1022 (1905); Pozzi-Escot, *Compt. rend.*, 435, 1334 (1907).

³ Pozzi-Escot, *Ann. chim. anal. chim. appl.*, 13, 390 (1908); 14, 207 (1909); Bollenbach, *Z. anal. Chem.*, 47, 690 (1908).

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A Lubricant Insoluble in Organic Solvents

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In working with organic solvents it is occasionally necessary to lubricate a stopcock or ground-glass joint in such a manner as to maintain a vacuum or a gas-tight seal and at the same time withstand the solvent action of the liquid. Under such conditions lubricants containing petroleum grease or rubber are as a rule useless on account of their solubility in the solvent and inorganic lubricants are often unsuitable due to separation of a constituent, reaction with the solvent, solubility or freezing.

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A solution of dextrin in glycerin is occasionally recommended² as a lubricant under the special conditions mentioned. The insolubility of this material in many organic solvents, as well as the high viscosity and slightly adhesive quality, renders this mixture suitable where a gas-tight seal is needed but where the frequent turning of a stopcock is unnecessary. The writers have found that the addition of mannitol in proper amount imparts the correct lubricating quality and renders this lubricant practically indispensable in certain types of work. For general use the lubricant may be prepared as follows.

Mix thoroughly 25 g. of anhydrous glycerin, 7 g. of dextrin and 3.5 g. of chemically pure *d*-mannitol until a thick paste is obtained. Heat carefully with constant stirring until the solid material is dissolved and the solution just begins to boil. A small amount of water is lost. Cool the clear, colorless or sometimes slightly turbid liquid with occasional stirring to room temperature. The liquid becomes highly viscous and finally acquires a lustrous white or opalescent appearance due evidently to the separation of part of the mannitol in a finely divided state. This preparation has excellent lubricating qualities as well as the body and adhesiveness suitable for most purposes. To increase the viscosity add more dextrin. To increase the fluidity add more glycerin. To impart the physical property of a greasy paste add a little more mannitol. Chemically pure *d*-mannitol is recommended, since commercial mannitol will not always yield the desired result. This lubricant is best stored in an ointment jar or kept in a desiccator, but exposure to laboratory air is not harmful.

The action of a number of solvents on this lubricant was tested as follows. The stopper of a small Erlenmeyer flask was lubricated so as to give a thin uniform film on both ground glass surfaces when the stopper was inserted. The stopper was removed, both lubricated surfaces were drenched with the solvent to be tested, and the excess of the solvent shaken or blown off. The stopper was then replaced in the flask and rotated to test the lubricating action. After repeating the operations of drenching and testing a number of times alternately the relative effects of the various solvents could be easily observed.

Tested in the manner described, the following solvents had no detectable effect, or at most a very slight and negligible effect: acetic anhydride, acetophenone, benzaldehyde, benzene, bromobenzene, carbon bisulfide, carbon tetrachloride, chlorobenzene, tetrachloroethane, cyclohexane, ethyl acetate, ethyl acetoacetate, ethyl bromide, ethyl carbonate, ethylene dichloride, methyl acetate, methylaniline, nitrobenzene, nitromethane, petroleum ether, diphenyl ether, toluene, *o*-toluidine, turpentine, *o*-xylene.

The following solvents had a slight effect, not, however, sufficient to prevent the use of the lubricant provided the latter is renewed when

² Iredale, *Phil. Mag.*, **45**, 1097 (1923).

necessary: acetaldehyde, acetone, acetyl chloride, amyl acetate, amyl nitrate, benzoyl chloride, *n*-butyl ether, diethyl ether, methylene chloride.

The solvent or disintegrating action of the following was sufficient to prevent or greatly hinder the use of the lubricant: aniline, acetic acid, tertiary amyl alcohol, benzyl alcohol, *n*-butyl alcohol, tertiary butyl alcohol, ethyl alcohol, methyl alcohol, diethylamine, ethylene chlorohydrin, ethylene glycol, formic acid, propionic acid, pyridine, quinoline, water and solvents containing water. In general, therefore, water, alcohols, aliphatic acids and to a lesser extent certain amines and nitrogen containing heterocyclic compounds prevent the use of the lubricant.

Before lubricating a stopcock with this preparation, petroleum and rubber grease should be entirely removed by means of benzene or acetone and the stopcock should be thoroughly dried. After applying a thin film of the lubricant, a stopcock will remain gas tight even when frequently turned in the presence of solvents of the first group mentioned above. With a liquid-air trap in the line to remove any water vapor evolved, a stopcock lubricated as described will hold a good vacuum. In gas analytical operations where the presence of petroleum grease was thought to cause error by absorbing constituents such as ether vapor, the glycerin-dextrin-mannitol lubricant has been used with success. Water dissolves the lubricant readily and may therefore be used to remove it when desired.

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The Probable Non-Existence of Normal Tribasic Aluminum Soaps Such as Aluminum Tripalmitate

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Aluminum soaps are articles of commerce used in several industries; they are even listed in most catalogs of pure reagents, and they have frequently been employed in scientific work.¹ Nevertheless, after repeated purchases and attempts to prepare aluminum tripalmitate and other tribasic aluminum soaps, we have come to the conclusion that the product is a mechanical mixture from which an appreciable proportion of free fatty acid is at once dissolved by ether, leaving behind a monobasic or at most a dibasic soap such as a dipalmitate, even when prepared and extracted in the complete absence of moisture. For example, Kahlbaum's aluminum tripalmitate yielded 50% of its fatty acid content to ether dried over sodium. A sample of aluminum palmitate obtained from Eimer and Amend contained only one equivalent of fatty acid to three equivalents of aluminum.

Aluminum soaps are usually prepared from aqueous solution by pre-

¹ For example, in emulsions of water with other solvents, in studies of swelling, etc.