HYDROGEN PEROXIDE SOLUTIONS.*

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Having noticed that the retail prices of different commercial brands of hydrogen peroxide varied a great deal, and, knowing that department stores and five and ten-cent establishments gave druggists considerable annoyance by selling certain brands at a ridiculously low price, I determined to investigate the different brands on the market, and I also did some experimental work to determine the best condition for keeping this product and to determine the rate of deterioration when kept under unfavorable conditions. My assistant, Mr. Fisher, and myself have conducted a series of experiments to determine this and have assayed samples from a number of different commercial brands, and this paper has to deal with the results of these experiments and assays.

It might be in order at this time to give a very brief history of the introduction of hydrogen peroxide to the world of medicine, and to note the causes for its rapid rise in importance as a medicinal agent, and as a useful commercial article.

The history of hydrogen peroxide is that of a chemical curiosity rapidly becoming so useful that it can be found in nearly every household, and so important that we have come to feel that it is next to impossible to get along without it.

In 1818 Thenard, a French chemist, first discovered hydrogen peroxide by treating barium peroxide with hydrochloric acid. The barium peroxide was made by heating barium oxide to a high temperature in air. The energy given to the barium oxide by the heat was transferred to a molecule of water, and instead of remaining H_2O it became H_2O_2. It has been prepared in a pure state by two methods, freezing and distillation under reduced pressure. In the pure state it is a thick, clear, colorless liquid of specific gravity about 1.5. This liquid is quite dangerous in that a number of things may cause it to explode and lose its excess of oxygen with violence. Even particles of dust have done this, and many severe explosions have occurred in laboratories where it was prepared.

The product that we are familiar with is far from dangerous, as we usually obtain it in about 3 percent solution in water, and in this condition it loses all its explosive force, while it still retains its antiseptic properties.

Hydrogen peroxide may be prepared in several ways, but the most common method of preparation is that of treating a metallic peroxide with an acid. Barium peroxide is used probably more than any other metallic peroxide. A number of acids have been used for this purpose, as sulphuric, hydrofluoric, hydrofluosilicic, all of which give insoluble precipitates with barium. We can readily see how the last two acids would be objectionable in the preparation of a medicinal hydrogen peroxide, as the solution might contain fluorine, but in the hydrogen peroxides used in bleaching, these methods are very satisfactory, as any fluorine they may contain will increase the efficiency of the bleaching properties of the solution. In the method given in the Pharmacopoeia of 1890, phos-

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phoric acid was used, but this acid is very expensive and the Pharmacopoeia of 1900 did not specify any method, therefore it can be made in any way the manufacturer sees fit to use, provided it corresponds to the tests given in the Pharmacopoeia.

Not all metallic peroxides will give this reaction when treated with an acid, e. g., manganese dioxide, when treated with hydrochloric acid, gives manganese chloride and free chlorine; sodium peroxide, treated with an acid, usually gives a salt of that acid, water, and free oxygen. However, if small amounts of sodium peroxide are added to a weak solution of hydrochloric acid, hydrogen peroxide is formed. This may be a possible explanation of the method used in preparing the cheaper peroxides, as nearly all of them contain sodium and chlorides, and it may be that a commercial sodium peroxide is used in their manufacture.

The importance of hydrogen peroxide is due to its power as an antiseptic and bleaching agent, which in turn is due to its strong oxidizing properties, it decomposing into water and nascent oxygen, the nascent oxygen being the antiseptic and bleacher. It has long been known that a strong oxidizing agent is a good antiseptic, the oxygen destroying the germs by oxidizing them. Chlorine, bromine and potassium permanganate have all been used for this purpose, but hydrogen peroxide has nearly displaced them, as it is a safer and more convenient agent to use.

When hydrogen peroxide comes in contact with blood, pus, or decayed tissue, there is an effervescence due to the exudation that is taking place. This effervescence is especially marked when hydrogen peroxide comes in contact with blood. This has led many people who are not familiar with it to feel that hydrogen peroxide is a dangerous solution. I have known laboring men, using this solution to dress wounds on the limbs of their horses, to rush quickly for soap and water and remove the excess of the solution, fearing that they would be injured by it. I suppose this was due to the fact that they were familiar with phenol, bichloride of mercury, etc., and knew that they were dangerous, and reasoning by analogy, thought that any agent that would cause such an effervescence, must be most powerful and therefore dangerous. The fact that it is not dangerous and is yet a powerful antiseptic explains its great use.

No solution of hydrogen peroxide is valuable unless it will retain its strength, and of two samples, both of which are pharmacopoeial, the one that will retain its oxidizing power the longer, is the one that pharmacists should recommend. A number of solutions of hydrogen peroxide do not retain this power and the manufacturers find it necessary to add something to preserve them. It has long been known that this solution is more stable in an acid solution than in an alkaline or neutral solution, therefore all solutions are acid in reaction. The U. S. P. limits the amount of acid that may be used, and no solution is pharmacopoeial that requires more than 2.5 cc. of N/10 potassium hydroxide to neutralize 25 cc. of the solution. It is surprising to find that many of them have a higher acid content than is allowed by the U. S. P. By accident it was found that acentanilid would aid in preserving these solutions. A chemist was attempting to form a combination between acetanilid and hydrogen peroxide and was unsuccessful in this attempt, but noticed that the sample containing acetanilid retained its strength much longer. This was a trade secret for years, but now it is known to all and nearly

all manufacturers use it as a preservative, usually of the strength of 3/16 gr. per fluid ounce. The chemistry of the action of acetanilid in this connection is not understood, and it stands out as one of the things that men have learned experimentally and that chemists are not yet able to explain. The small amount of acetanilid used has no injurious effect and adds wonderfully in preserving the solution. Some claim that the acetanilid acts as an antiseptic, but I do not believe that this has been proven. We have on the market today a number of brands of hydrogen peroxide that do not use acetanilid to preserve them, and yet they do not deteriorate more rapidly than do solutions that do not contain acetanilid, therefore it seems that acetanilid is not always necessary to preserve this solution.

First, I wish to call your attention to the chart showing the results of keeping this solution under different conditions.

Considering the first two results, it is made plain that a solution kept in a bottle stoppered by cotton retains its strength much better than when contained in a bottle stoppered with cork. You will note that this is true in a number of cases shown on this chart. In some cases the solution gained in strength. I think that the explanation of this is that with a cotton plug there is quite free access of air and the water evaporates more rapidly than the hydrogen peroxide decomposes.

If the container is stoppered with cotton, the amount of hydrogen peroxide is not increased, but the percentage of it is increased because of the loss of water.

I wish to call your attention to the fact that solutions that were kept in the basement were more stable than those kept in diffused light, and those kept in diffused light were much more stable than those kept in the sunlight. Of two samples kept in the sunlight, one lost 98 percent and the other 99.9 percent. While the one kept in the amber bottle in the sunlight lost but 65 percent.

It seems to me that these facts lead us to conclude that pharmacists should keep their stock of peroxides in the basement and display but few bottles to the trade.

The fact that this solution decomposes so rapidly in the sunlight, should be impressed upon the buyer and they be instructed to insert a plug of cotton in the neck of the bottle and store it in a dark, cool place.

You will note the wonderful difference in rate of decomposition between solutions in colorless bottles and those in amber colored bottles, especially if those bottles are exposed to the direct rays of the sun, yet there are manufacturers today who put out their products in colorless bottles.

Many more interesting facts might be noted from the study of the "Loss %" column in this chart, but I will leave that for your consideration later.

Turning your attention to the results of the assays of different commercial brands of peroxide as shown in Chart B, you will note that most of them are nearly U. S. P., as far as the strength of the solutions are concerned. In justice to the Albany Chemical Co. and to Squibbs & Sons, I wish to explain that the sample from the Albany Chemical Co. was purchased in open market and I have no way of knowing how old it was before we assayed it; and that in case of the sample from Squibbs & Sons, we had it in our basement for two years, therefore it is not fair to them to compare this sample with a fresh one. I bring it in here to illustrate that some solutions of hydrogen peroxide do not keep well unless a preservative is used. You will note that Squibb & Sons do not use a preservative.

EFFECT OF VARYING CONDITIONS ON SOLUTIONS OF HYDROGEN PEROXIDE.

Sample	Basement	Diffused Light	Sunlight	Nov. 25 1911	Jan. 11. 1912	Mar. 12	May 7	Loss %
Eimer & Amend. Hydrogen Peroxide U. S. P. Contained 3/16 gram acetanilid. Purchased Sept. 24, 1911. (In colorless bottle unin-closed.)	Colorless bottle cotton plug.			3.19	2.70	2.86	2.99	6.6
	Colorless bottle cork.			3.19	2.60	2.50	2.35	16.3
		Colorless bottle cotton plug.		3.19	2.68	3.00	out	6.00
		Colorless bottle cork.		3.19	2.36	1.94	1.39	56.6
		Amber bottle cork.		3.19	2.38	2.05	1.58	50.5
			Colorless bottle cotton plug.	3.19	0.36	0.07	0.06	98.00
			Colorless bottle cork.	3.19	0.11	0.009	0.004	99.9
			Amber bottle cork.	3.19	2.32	1.76	1.12	65.
					Jan. 12	Mar. 12	May 7	
Oakland Chemical Co. Dioxogen. Purchased Sept. 24; claimed 12 vol. H_2O_2.	Colorless bottle cotton plug.				3.48	2.98	3.83	9% gain
	Amber bottle cork.				3.48	3.58	2.98	14.4
		Colorless bottle cotton plug.			3.48	2.89	1.28	63.2
		Amber bottle Cork.			3.48	2.50	1.35	61.2
Marchands Medicinal. Hydrogen Peroxide. (Colorless bottle in carton.)	Colorless bottle cotton.				2.05	2.11	2.24	9.2 gain
	Amber bottle cork.				2.05	1.81	1.48	28.
		Colorless cottons.			2.05	2.11	out	
		Amber bottle cork.			2.05	1.67	1.22	40.5
Marchands Hydrozone. 30 vol. H_2O_2. (Colorless bottle in carton.)	Colorless bottle cotton plug.				2.48	2.97	out	20 gain
	Amber bottle cork.				2.48	2.31	out	7.0
		Colorless bottle cotton plug.			2.48	2.72	out	10 gain
		Amber bottle cork.			2.48	1.90	out	23.42

STUDY OF COMMERCIAL BRANDS OF HYDROGEN PEROXIDE.

Samples	May 10	May 27	Salts	Assay Acidity	Solids
Parke, Davis & Co. Hydrogen Peroxide, 3% H_2O_2 3/16 gr. acetanilid per fluidounce. Guaranteed U. S. P. Full strength on leaving our laboratory.	2.98		Trace of sulphate	4 cc. of N/10 KOH to 25 cc. of solution	U. S. P.
Hydrox Consumers Co. 3/16 gr. acetanilid per fluidounce. Represents the highest chemical skill in producing absolute purity and potency. Conforms to the U. S. P. requirements, having the additional advantage of potency. Last drop as potent as the first.	2.61	2.5	Heavy with sulphate and chlorides	47 cc. of N/10 KOH to neutralize 25 cc. of sol.	U. S. P.
Albany Chemical Co. Hydrogen Peroxide, 3% H_2O_2, 1/6 gr. acetanilid per fluidounce. Guaranteed to be unsurpassed in purity, strength and keeping qualities.			Trace of sulphate Excess of chloride	U. S. P.	U. S. P.
Western Peroxide Co. Hydrogen Peroxide. 10 vol. H_2O_2. U. S. P. H_2O_2. 3/16 gr. acetanilid per fluidounce. 6 oz. 15c. Guaranteed. Serial No. 25940.	2.5	2.39	Trace of sulphate Excess of chloride	4.05 cc	U. S. P.
Squibbs & Sons. Hydrogen Peroxide (two years old). 10 vol. H_2O_2, made by special Squibbs process.	0.67		Trace of sulphate Excess chloride	39.4 cc.	U. S. P.
Hydrox Hydrogen Peroxide, Hydrox Chemical Co. 10 vol. H_2O_2. U. S. P. 3%. 3/16 gr. acetanilid per fluidounce. Last drop as potent as the first. Serial No. 2685.	2.68	2.5	Trace of sulphate	U. S. P.	U. S. P.
Hydrox. (Same as above. Sold at 9c per pint on sale. Regular price 25c.)	2.82		Heavy with chloride and sulphate	U. S. P.	U. S. P.
Oakland Co. Dioxogen. 12 vol. H_2O_2.	3.55		Trace of chloride	U. S. P.	U. S. P.
Menthymine. Hydrogen Peroxide. Billings, Clapp & Co. 3/16 gr. acetanilid per fluidounce. For the toilet. An improved preparation representing all the valuable properties of the ordinary peroxide. (Contained menthol and was colored.)	0.24		Trace of chloride	30 cc. of N/10 KOH to neutralize 25 cc. of	Little higher

You will notice that a great many of these samples contain an excess of chlorides or sulphates, although the U. S. P. gives tests for these salts. You will also notice that in some cases the acidity is much higher than that allowed by the U. S. P., namely 2.5 cc. of N/10 potassium hydroxide to neutralize 25 cc. of solution. Again I wish to say, in justice to Squibb & Sons, that this sample tested much higher in acid content than did their samples assayed by the government chemists. I do not know whether this was due to its being an old sample or not.

You will notice that menthymine was very low in hydrogen peroxide content and it contained menthol and a coloring agent.

It is interesting to note the difference between the claims of companies as shown in the column marked "Samples" and the result of the assay of their samples.

In conclusion, I wish to state that many solutions of hydrogen peroxide on the market today are very good, although they do not meet all of the tests of the U. S. P., and I do not believe that pharmacists can afford to carry only the high-priced standard varieties, and look with contempt upon the cheaper varieties carried by department stores and five and ten-cent establishments. I asked my students to purchase samples of hydrogen peroxide to assay, and two of them brought in samples of the same product manufactured by the same company; one had obtained a two-ounce sample at a drug store for fifteen cents, the other a four-ounce sample at a department store for ten cents. Such deals as these lead the laity to believe that pharmacists are charging an excessive price for their material. It would seem to me that it would be better to carry a good U. S. P. article and charge enough for it to make a reasonable profit, and also carry a little of the cheaper, inferior article and display them together, meeting the department store on the price of the cheaper article, and then explain to the purchasing public why one article is better and consequently more expensive than the other. I believe you will sell but little of the cheaper grade of material, and you will hold the confidence of your customers.

THE MAN WITH INITIATIVE.

All the great prizes of this world are reserved for those who possess initiative.

Initiative has been defined by one of our most versatile writers as "doing the right thing without being told, and the next best thing, to do the right thing after being told once." But we want a more practicable and understandable meaning of this marvelous quality.

Let us say that any individual who always is, to a large degree, helpless, depending upon some force outside of himself to bring out his usefulness, lacks initiative. A man without initiative is a man that cannot get up steam, pick out a course and steer away to his destination without the help of somebody else.

But the man with initiative is a live wire. This is the kind of men for whom good positions are going begging every day.—*Western Druggist.*