

The pressures employed were 246 to 351 kg. per sq. cm. (3500 to 5000 pounds per square inch), and the experiments indicated probable reaction at lower pressures.

Though pure carbon monoxide facilitated final recovery of unchanged amine, it did not disclose sufficient advantage to compensate its greater expense. Water gas seems to offer the best source of inexpensive reactant.

Various runs were made to determine the optimum ratio of amine and solvent. Since both the solvent and unchanged amine are easily recoverable for reprocessing and because yields are substantially high, this pressure method seems of technical importance. Its further development and application for formation of fuchsin and other dyes will be studied.

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Persulfate as a Soap Bleach

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In bleaching palm oil soap, 0.5 per cent of potassium persulfate based on the anhydrous soap content gives over 90 per cent reduction of color at 20 per cent soap concentration, or 85 per cent reduction at 50 per cent concentration. The soap is bleached after saponification and salting out. Increase of persulfate concentration has little effect. There is but little temperature effect between 80° and 100° C. with a slight maximum indicated at 90°. Large amounts of excess alkali lower the effectiveness, but moderate excess has no effect. The rate of addition of the persulfate is of little importance.

Catalysts known to influence the stability of hydrogen peroxide proved to have no beneficial effect and in some cases were detrimental. At the same concentration potassium persulfate is much more effective than hydrogen peroxide or sodium perborate.

The effectiveness of persulfate as a bleach for tallow is lower. The green color of olive-oil foot soap is altered to, or replaced by, an orange color with relatively high concentration of persulfate. Soap from good-quality olive oil is bleached. No important degree of bleaching of corn oil, cottonseed oil, or coconut oil soap is obtained.

ALTHOUGH persulfates have been reported to be effective bleaching agents for soap, their use for this purpose has not developed on a commercial scale in this country. Such use originated in Germany and has been adopted to a substantial extent there. A number of proprietary bleaching agents on that market, known by such names as Peroxol, Palidol, and Persofol, contain persulfate as their chief ingredient. Some ammonium persulfate is often present (10). This method of bleaching, however, has apparently not been able to compete successfully with other methods in use in this country.

PREVIOUS WORK

The bleaching of soap with persulfates was patented in 1906 (11). The process is described as being particularly advantageous for bleaching soaps made from linseed oil, palm oil, cottonseed oil, neat's-foot oil, and impure olive oil. According to the example given, 0.5 per cent of persulfate on the basis of the fat used is added to the soap batch during boiling. Palidol has been reported in the literature to give good results for bleaching tallow and cottonseed oil soaps (1). A similar procedure has been described (9) for the use of potassium persulfate in bleaching a soap stock consisting of tallow, bone grease, palm kernel oil, and peanut oil fatty acids. A series of experiments on the use of persulfate in the form of a trade product called Peroxol have been reported, in which both hard and soft soaps were bleached (2). In all of these

the persulfate was added with alkali to the boiling soap previous to salting out. In later experiments (4) it was found that the use of the persulfate in saponification always produced an odor of chlorine when the soap was salted out. Decomposition of persulfate was apparently incomplete. It was therefore recommended that the persulfate be added to the strongly alkaline soap just after salting out, at a temperature just below boiling.

In many cases the bleaching effect has been reported as followed by afterdarkening (6) in some cases in the presence of excess persulfate, in other cases in its absence. This indicates that each type of soap stock is a separate problem.

A number of other experimenters (3, 7, 8) have dealt with improving the bleaching effect of persulfate by using some other material with it—subsequent treatment with a reducing agent, for example. Persulfate and hydrogen peroxide have been used together (5).

In these and other references the procedures described vary. There are apparently no accepted optima as to temperature,

time of treatment, type of agitation, concentration of persulfate, and other factors which will give the best results. These factors were therefore investigated.

EXPERIMENTAL METHOD

Preliminary experiments were carried out with soaps of various fats. Palm oil soap was selected as the standard material for the work because it showed the greatest difference in color between the bleached and unbleached soap. The

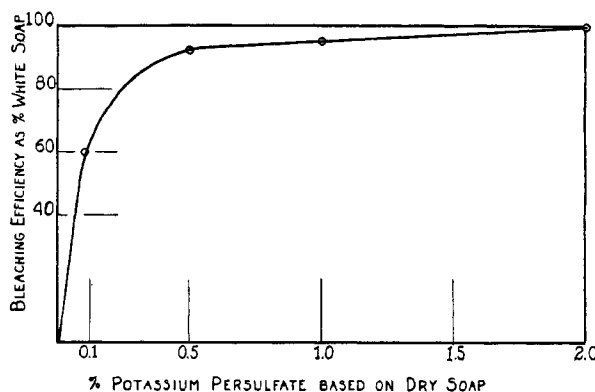


FIGURE 1. EFFECT OF CONCENTRATION OF PERSULFATE

soap used was prepared in the laboratory by saponifying palm oil with 15° Bé. caustic soda, and salting out with sodium chloride. The soap for the entire series of experiments was made from the same batch of palm oil so that there were no variations in the original color of the soap, which was a dark orange shade. Analysis of the soap showed it to be completely saponified and to contain approximately 60 per cent anhydrous soap.

Experimental handling of soap in a concentration above 20 per cent is difficult because of foaming. Therefore the main part of the work was carried out with this 60 per cent

soap dissolved in water to give a 20 per cent solution. The amounts used normally contained 100 grams of anhydrous soap. A series was run later to show the effect of varying the concentration.

The apparatus in which the bleaching was carried out was analogous to the open kettle commonly used in soap plants, which provides for agitation by means of jets of live steam. A flask of suitable size was surrounded by a heating bath of brine. A steam line led to the bottom of the flask which provided agitation of the contents and maintained the temperature at 100° C. This was equipped with a trap to prevent condensation in the line and consequent relatively large increase in the volume of solution contained in the flask.

The persulfate dissolved in water was added to the soap solution in the flask at a constant rate, calculated so that the time for addition would be 30 minutes. After all the persulfate had been added, the solution was agitated for 30 minutes longer to insure complete utilization of the persulfate. In all cases a suitable test showed absence of residual persulfate. The bleached soap was then salted out and stored, without being washed, in tightly stoppered glass bottles. Samples were withdrawn from these for colorimetric comparison with a series of standards to show the degree of bleaching that had occurred.

METHOD OF COMPARISON

Some difficulty was experienced in preparing samples for colorimetric comparison as the bleached soap tended to give cloudy solutions in several solvents tried. It was found, however, that satisfactory comparison could be made by using solid solutions in glycerol of both the standards and the test specimen, the solutions being made up to contain 10 per cent by weight of anhydrous soap. Such a solution of commercial white soap was selected as the standard for optimum removal of color, as it was transparent and practically colorless. A series of standards was then made up consisting of mixtures in varying proportions of the white soap solution and a similar glycerol solution of the unbleached experimental soap, a total soap content of 10 per cent being uniformly maintained. The proportions varied from a ratio of 98 per cent white to 2 per cent experimental soap in the lightest standard to 40 per cent white to 60 per cent experimental soap in the darkest. The standards thus showed a range of colors between the color of the original unbleached soap solution and the substantial absence of color of the white soap solution. These standards were placed in tubes which were sealed with paraffin. To determine the efficiency of the bleaching operation, a glycerol solution containing 10 per cent of the anhydrous bleached soap was made up and compared with the series of standards against a white background. The degree of bleaching obtained is expressed in terms of the percentage of white soap in the standard it matched. In some cases slight cloudiness occurred in the test specimen. This was cleared up by heating, in which case the standards were heated to the same temperature.

When not in use the color standards were protected from exposure to light. They were checked at the end of 3 and 5 months and found to be unchanged.

DETERMINATION OF OPTIMUM CONDITIONS

CONCENTRATION OF PERSULFATE. A commercial potassium persulfate was used in all experiments. It was substantially pure. The ratio of quantity of potassium persulfate used to the degree of bleaching obtained was the first variable studied. With all other factors maintained constant as far as possible, the original palm oil soap was bleached by the process described with amounts of persulfate varying from 0.1 to 2.0 per cent by weight of the amount of anhydrous soap to be bleached. The bleached soap obtained in each case was compared with the series of color standards, giving the results shown in Figure 1. Based on these results 0.5 per cent was taken as the optimum concentration of persulfate, since this showed removal of over 90 per cent of the color and higher concentrations increased the bleaching efficiency but little.

TEMPERATURE. Using a concentration of 0.5 per cent potassium persulfate and with other variables constant, the soap was bleached by the process described, at different temperatures ranging from 70° to 100° C. In order to obtain the temperatures desired below 100° C., steam could not be used for agitation in these runs. Agitation by mechanical means was substituted. While there is no great difference in the bleaching effect over this range, as shown in Figure 2, the optimum temperature appears to be 90° C. Since the difference in degree of color removal between that temperature and

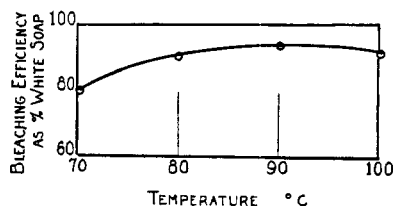


FIGURE 2. EFFECT OF TEMPERATURE

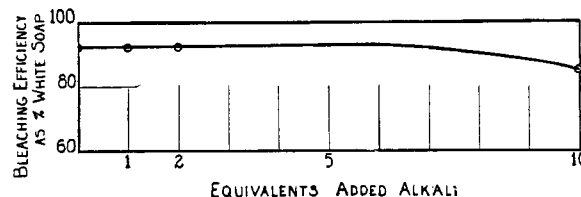


FIGURE 3. EFFECT OF EXCESS ALKALI

100° was very slight, 100° was adopted as the standard temperature for later runs because of the greater convenience of using steam for agitation and because of the parallelism to plant operating conditions.

FREE ALKALI. Since persulfate reacts during the bleaching process to give free acid, some alkali must be added to prevent decomposition of the soap and formation of free palmitic acid. The reaction is:



As excess alkali might have some effect on the bleaching efficiency, the amount of alkali added was studied as a variable and runs were made with varying quantities of sodium hydroxide present. These quantities varied from none at all to an amount ten times that equivalent to the sulfuric acid liberated by the amount of persulfate used. Results are shown in Figure 3. It is apparent that the bleaching effect remains unaffected either in the absence of alkali or in the presence of a small excess of alkali. A large excess, however, substantially decreases the bleaching efficiency. In the commercial use of persulfate for bleaching it would therefore be necessary to control the amount of excess alkali rather carefully in order to obtain complete neutralization of liberated acid and at the same time avoid the use of a large excess of alkali. As a standard procedure in these experiments an amount of sodium hydroxide equivalent to twice the amount of acid liberated was adopted.

RATE OF ADDITION OF PERSULFATE. On the theory that too rapid addition of the persulfate to the soap might result in a loss of some of the available oxidizing strength, runs were made in which the rate of addition of the persulfate was varied. In one run all the persulfate was added at once, in another it was added gradually over a period of 15 minutes, and in another it was added over a period of 30 minutes. The soap was bleached to the same color in all three cases. This result indicates that the decolorization reaction utilizes all the available oxygen of the persulfate as fast as it is liberated. Since an addition period of 30 minutes had been used in prior experiments, it was continued for the sake of uniformity.

ADDITION OF STABILIZERS AND ACCELERATORS. Compounds such as thymol, hydroquinone, and stannic phosphates are known to be stabilizers for hydrogen peroxide. Titanium and iron salts are known to catalyze its decomposition. There was a possibility that these substances might have a similar effect with potassium persulfate. Runs were therefore made with the addition of these materials in concentrations of 0.1 and 0.01 per cent by weight of the soap bleached on a dry basis. Positive results were obtained only with hydroquinone, which decreased the bleaching efficiency. This apparent effect may have been due to the formation of colored compounds of hydroquinone.

CONCENTRATION OF SOAP. To handle more concentrated soaps, they were heated in a glycerol bath and stirred by hand, to avoid foaming. As contrasted with over 90 per cent color removal at 20 per cent soap concentration, 0.5 per cent of persulfate removes only 85 per cent of the color at 50 per cent soap concentration. This degree of color removal leaves a distinguishable yellow tinge in the bleached soap. Variations in the method and time of adding persulfate at this higher soap concentration were without effect. The optimum effect at a lower concentration is therefore indicated.

AFTERDARKENING

A limited number of observations were made on this property. As typical ones, soaps originally showing a color of 92.5 stood in the dark for 2 months and again read 92.5. The same soaps in the light bleached to 95 in that time. After 5 months the results were the same. A soap having a value of 82½ bleached in 33 days in the light to 90. One sample having ten times the amount of alkali to be equivalent to the persulfate was the only case of afterdarkening noted. In that case the effect was ascribed to excess of alkali rather than to persulfate which, by test, was absent at the conclusion of all bleaching experiments.

COMPARISON WITH OTHER BLEACHES

Palm oil is commercially bleached by agitation with chromic and sulfuric acids or by exposure to sunlight. The soaps from palm oil can be bleached with hydrogen peroxide or with sodium perborate. The latter two would be directly comparable in technic to the use of persulfate.

TABLE I. COMPARATIVE BLEACHING EFFICIENCY OF PERSULFATE, PEROXIDE, AND PERBORATE

BLEACHING AGENT	CONCN. OF SOAP TO BE BLEACHED ON DRY BASIS	DEGREE OF BLEACHING OBTAINED
	% by wt.	%
Potassium persulfate	0.5	92.5
Hydrogen peroxide ^a	0.5	40.0
Hydrogen peroxide ^b	0.5	40.0
Hydrogen peroxide	1.0	60.0
Hydrogen peroxide	2.0	80.0
Hydrogen peroxide	5.0	92.5
Sodium perborate	0.5	40.0

^a No alkali added.

^b Alkali equivalent to that in standard procedure added.

Using the determined optimum conditions and following the standard procedure outlined, a series of runs was made using hydrogen peroxide or sodium perborate in place of the potassium persulfate. In some runs the amount of peroxide or perborate was the same as the optimum amount found for the persulfate—that is, 0.5 per cent by weight of the anhydrous soap. In other runs higher concentrations of peroxide were used. The results obtained are shown in Table I.

These results show positively that persulfate is superior to either peroxide or perborate for bleaching palm oil soap under the conditions used.

EFFECT ON OTHER SOAPS

The standard procedure arrived at in experiments with palm oil soap was also applied to a number of other kinds of soap. With a tallow soap made from a low-grade house grease only a part of the color, not mechanically removable in the saponification process, was bleached. The effect was similar to that of peroxide and of perborate in the same concentration on this soap.

When applied to a boiled-down cottonseed oil foot soap of high color and rank odor, persulfate bleaching had relatively little effect. This soap appears to contain a brown pigment and a yellow-to-orange pigment. The first can be removed by the process but the second cannot.

Persulfate gave a measurable bleaching effect on a soap from good-grade olive oil, which was relatively light in color. Owing to this original light color the effect of the bleaching was scarcely distinguishable. Hydrogen peroxide and perborate did not give measurable bleaching.

With an olive-oil foot soap a change of color rather than a bleaching effect resulted. The original soap was dark green, which was lightened to some extent by 0.1 per cent persulfate. Increase of the persulfate to 0.5 per cent gave a greenish yellow color, and further increase produced an orange color. One possible explanation is that a mixture of green and yellow pigments is present in this soap, of which only the green is removed by the bleach. In that case presumably the yellow is carotinoid pigment which is deepened in color by the persulfate. Alternatively the green pigment may be changed by oxidation to yellow or orange. The literature on the subject of oxidation of such pigments provides no satisfactory explanation of this behavior. Peroxide and perborate show only the slight degree of bleaching given by 0.1 per cent of persulfate.

No bleaching effect could be obtained in treatment of coconut oil soap. Corn oil soap showed only a slight reduction of color with 1 per cent of persulfate.

ACKNOWLEDGMENT

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