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Flotation of Particles Suspended in Lye by the Decomposition of Hydrogen Peroxide

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Abstract

The spontaneous decomposition of H_2O_2 in concentrated caustic soda solutions produces bubbles that can be used to remove impurities from industrial mercerizing liquids. Experiments proved that different model substances can be floated out of concentrated lyes. The separation of crystalline Na_2CO_3, the removal of vat dyes, and the removal of mixtures of vat dyes with soda were investigated. Surfactants of different ionic activity were used to improve the purification process. If crystalline Na_2CO_3 is present, pigments which otherwise can hardly be separated by flotation can be removed from the lye. Pigments of naphthol dyes can be floated out of the lye by the use of H_2O_2 alone. Cotton dust, which serves as a model substance for fiber particles, can be separated almost completely by the O_2 bubbles generated through the H_2O_2 flotation process.

INTRODUCTION

The textile industry uses large quantities of NaOH for mercerizing cotton goods. In many mills diluted spent lyes are recovered by evaporation until a concentration of 250 to 350 g/L NaOH is reached. Such concentrated spent lyes are often heavily contaminated by dyes (mercerization of colored woven goods), washed out sizing agents (mercerization of gray-state goods), fiber fragments, dust, and soda (produced from the CO_2 of the air), so that recycling is not or only partially possible (*1*).

To remove impurities from lyes, several methods have been proposed and tested, among them sedimentation (*2*), centrifugation, filtration, and electroflotation (*3*). In earlier processes the bubbles needed were led through or produced in the lye by mechanical [injection of air (*4–7*), dissolved air flotation (*8*, *9*)] or electrolytical methods [electroflotation (*3*, *10–12*)]. A new efficient method is the purification of lyes by chemical flotation (*13–16*). In this process the bubbles are generated by the spontaneous decomposition of H_2O_2 in an alkaline solution (*17–24*):

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (1)$$

In the purification apparatus, lyes from industrial mercerization processes and model solutions were studied under various conditions. Spent lyes from industrial mercerization contain a mixture of different substances (NaOH, soda, salts, linters, dust, surfactants, natural dyes, synthetic dyes) and therefore standardization in an experiment is difficult. However, model systems make exact operating conditions possible.

The tests described here concern the removal of soda, synthetic dyes, and cotton dust from concentrated caustic soda (concentration range of 300–400 g/L NaOH). The influence of surfactants on the grade of removal was investigated by the addition of surfactant solutions. As cotton particles of short average length can be used as a model substance for fragments from cotton fibers, the removal of cotton dust from concentrated lye was investigated.

EXPERIMENTAL

In all flotation experiments, 50 mL graduated glass cylinders were used. Different quantities of 30 wt% H_2O_2 were added under stirring into a beaker with a 25 mL solution of the model substance (concentration of NaOH 300–400 g/L). The flotation effect takes place during retention in the glass columns (test series at room temperature and 50°C).

To remove Na_2CO_3 from concentrated NaOH solutions, model systems were prepared by adding concentrated soda solutions to concentrated NaOH solutions. Acidimetric measurements of the soda content in concentrated lyes gave only inaccurate results. Therefore, volumetric analysis was used to define the concentration of Na_2CO_3 by measuring the amount of CO_2 released after acidification.

The different vat dyes were dissolved by vatting in long liquor (16 mL/L

NaOH 38°Be, 6 g/L $Na_2S_2O_4$) and subsequently oxidized with H_2O_2 (0.1, 0.5, 0.8 mL), thus simulating a dyeing process to produce dye particles of a similar size and surface structure. Immediately after the H_2O_2 addition, concentrated NaOH is added. 25 mL of the dye solution (2 g/L) is mixed with 25 mL of 766 g/L NaOH caustic soda. The resulting mixture contains 1 g/L dyestuff and approximately 390 g/L NaOH. Due to the heat generated in the mixture and the high NaOH content, the H_2O_2 decomposes rapidly and starts the flotation of solid particles. To investigate the influence of temperature, the solutions were kept at 50°C or at room temperature until the decomposition of H_2O_2 was complete. Afterwards the foam containing dye particles was removed by suction. Vatting was effected by adding an excess of $Na_2S_2O_4$ to the dye. The amount of the dye was analyzed colorimetrically after dilution with a known volume of blank vat. By comparing the readings with the concentration of the theoretical dilution, the purification effect was calculated.

To investigate the influence of surfactants, first 2 mL of a surfactant solution (10 g surfactant/L) and then the concentrated NaOH solution were added to the oxidized dye. As surfactant additives dodecyl hydrogen sulfate-sodium salt (D, anionic), nonyl phenol polyethylene glycol ether (N, nonionic), and Hyamine 1622 (H, cationic) were used.

Simulating technical conditions, crystallized soda was produced in the lye by precipitating this compound from oversaturated solutions. 120 g/L soda was dissolved in the dye solution prepared as described above. Soda crystallizes when the dye solution is mixed with the concentrated lye. Again the flotation tests were carried out at room temperature and at 50°C.

Naphthol dyes are deposited on the fiber by coupling a water-soluble naphtholat with a water-soluble fast color (diazo compound) salt. The dye solution used for the flotation experiments had therefore to be produced by removing the pigments from the fiber (fixed naphthol 20–40 g/kg). The coupled dye particles are not chemically bound to the fiber and are of a form similar to those in the unpurified mercerizing lye (size distribution, surface structure, surfactant adsorption, etc.). Approximately 100 g of bleached knitware was dyed by the exhaust method with different combinations of naphthol and fast color salts. Table 1 gives the naphthol combinations used.

The different naphthols were impregnated and developed according to the manufacturer's recipes (Hoechst AG). After the dyeing process the goods were treated with boiling water containing 3 g/L soda to remove the badly fixed dyestuff. As dark shades were used, the proportion of coupled

TABLE 1
Coupling Combinations Tested (Hoechst)

Naphthol	C.I.	Fast color salt	C.I.	Shade
Naphthol AS-RS	37541	Fast navy blue RAS	37195	Navy blue
Naphthol AS-RS	37541	Fast red TR	37085	Red
Naphthol AS-SG	37595	Fast red B	37125	Black
Naphthol AS-S	37580	Fast bordeaux BD	37170	Bordeaux

badly fixed dyes was relatively high. After the soda treatment, the dye suspension was diluted to 250 mL and served as the basis for the flotation experiments.

12.5 mL of the dye solution and 12.5 mL NaOH (766 g/L) were mixed, and different amounts of H_2O_2 (30 wt%) were added. After mixing, the solution was kept at 30°C in a water bath. Approximately 5 h later the foam on the top was sucked off and 10 mL of the purified lye was neutralized with acetic acid (100%) and diluted to 50 mL. 5 mL of this solution was mixed with DMF to analyze the concentration of the dye colorimetrically.

The influence of an industrial surfactant (mercerization assistant) was measured by the addition of 0.1 mL Mercerol (Sandoz) to 25 mL of the test lye.

To analyze how cotton dust can be eliminated, parts of cotton fibers of an average length of 0.88 mm were mixed into caustic soda (350 g/L NaOH). Lye samples were treated with different amounts of H_2O_2 (0.25, 0.5, 1.0, 2.0%) at room temperature and at 50°C. To determine the cotton content, light transmission was measured at 436 nm. The calibration curve for interpretation was based on data received from light absorption measurements of lyes with a known cotton dust content.

RESULTS AND DISCUSSION

Figure 1 shows the removal of Na_2CO_3 from the Na_2CO_3–NaOH model systems, starting at different Na_2CO_3 concentrations in the lye. 1 vol% H_2O_2 was added.

Na_2CO_3 crystallization in a 350 g/L NaOH lye only takes place above a minimum concentration of approximately 38 g/L. This is the soda content measured after removing the solid Na_2CO_3 by flotation. Almost the total amount of crystallized soda is floated out. In industrial lyes it is

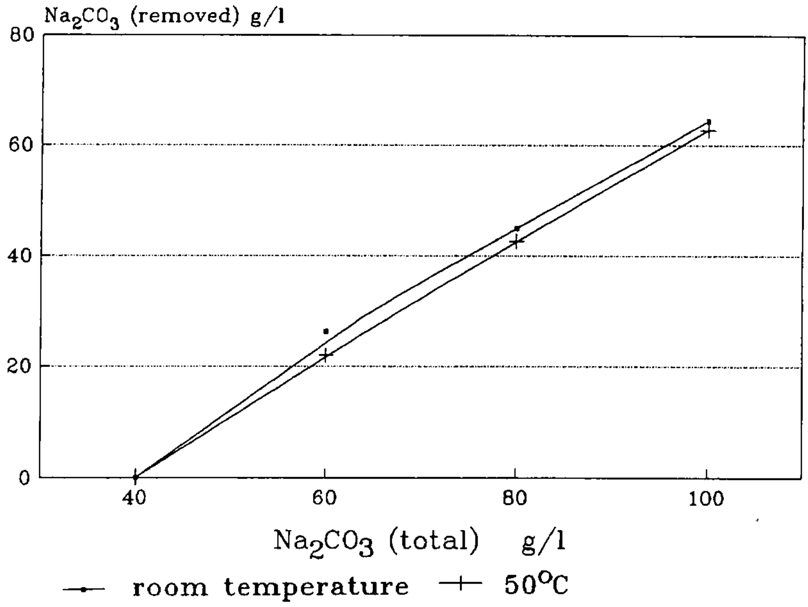

FIG. 1. Flotation of Na_2CO_3 at room temperature and 50°C.

often found that the Na_2CO_3 crystallized on the surface (NaOH taking up CO_2 from the air) adsorbs the dyestuff present in the lye. Therefore the flotation behavior of multisystems (e.g., soda and dye) is analyzed in comparison with one-component systems.

Flotation tests were made with vat dyes and naphthol dyes. The results of the vat dye systems are given in Tables 2, 3, and 4.

Experiments where only 0.1 mL H_2O_2 was added were used to differentiate the effect of oxidation of the dyestuff and purification by flotation due to an excess of H_2O_2. To determine the influence of the amount of H_2O_2 (volume of gas bubbles set free), 0.25, 0.5, 1.0, and 2.0 vol% H_2O_2 were added to the lye, corresponding to 0.25 to 2 L of releasable O_2 gas/L lye.

The following industrial dyes were used as model substances: Indanthrene yellow 3R (CI Yellow 11:1), Indanthrene red FBB (CI Red 10), Indanthrene dark blue DB (Mixture), Indanthrene navy blue G (CI Blue 16), Indanthrene brilliant green GG (CI Green 2), Indanthrene blue GC (CI Blue 14), Indanthrene grey CL (Black 31), and Indanthrene golden orange GG (CI Orange 26) (BASF). With two dyes (Indanthrene yellow

3R and Indanthrene red FBB), pigment particles could be removed without further additives. The results of the tests with these two dyes are given in Table 2.

As no direct flotation was possible with the other pigments, three different auxiliaries were added to improve dye removal. The results of the flotation experiments with the addition of surfactants are given in Table 3.

Based on the results with the dye-H_2O_2 systems, analyses were made as above, dealing with the removal of dye pigments in the presence of crystalline anorganic solids (Na_2CO_3, etc.), since such solids are found in industrial lyes.

Flotation experiments with the dyes given in Table 4 were undertaken when crystalline soda was present. Care was taken that this soda is of a similar form to that present in industrial lyes, where crystallization

TABLE 2
Flotation Tests with Vat Dyes (no further chemicals added)

Dye	H_2O_2 added for 50 mL	Dyestuff: Theoretical (mg/mL)	Dyestuff: Experimental (mg/mL)	Residue dye (%)
Indanthrene yellow 3R	0.5	0.084	0.005	6
	0.8	0.084	0.011	13
	1.0	0.046	0.009	20
Indanthrene red FBB	0.5	0.023	0.029	100
	0.8	0.046	0.017	37
	1.0	0.046	0.033	71

TABLE 3
Flotation of Vat Dyes in the Presence of Surfactants (D = dodecyl hydrogene sulfate-Na salt, N = nonyl phenol polyethylene glycol ether, H = Hyamine 1622)

Dye	Surfactant	H_2O_2 added for 50 mL	Dyestuff: Theoretical (mg/mL)	Dyestuff: Experimental (mg/mL)	Residue dye (%)
Indanthrene	D	0.5	0.046	0.043	94
dark blue	N	0.5	0.046	0.024	53
DB	H	0.5	0.046	0.012	27
Indanthrene	D	0.5	0.023	0.010	45
navy blue G	N	0.5	0.023	0.014	62
	H	0.5	0.023	0.012	50

TABLE 4
Flotation Tests with Crystallized Soda

Dyestuff	Amount of H_2O_2 (vol%)	Temperature (°C)	Removal (%)	Time (min)
Indanthrene brilliant green GG	0.25	20	29.7	100
	0.5	20	82.3	100
	1.0	20	72.7	100
	2.0	20	61.2	100
	0.25	50	87.1	40
	0.5	50	77.2	40
	1.0	50	56.9	40
	2.0	50	62.1	40
Indanthrene blue GC	0.25	20	—	150
	0.5	20	35.5	150
	1.0	20	36.8	150
	2.0	20	27.4	150
	0.25	50	—	160
	0.5	50	52.4	160
	1.0	50	44.2	160
	2.0	50	24.8	160
Indanthrene grey CL	0.25	20	27.7	160
	0.5	20	90.9	160
	1.0	20	85.5	160
	2.0	20	40.7	160
	0.25	50	92.4	100
	0.5	50	89.2	100
	1.0	50	85.3	100
	2.0	50	23.7	100
Indanthrene golden orange GG	0.25	20	—	120
	0.5	20	38.4	120
	1.0	20	31.2	120
	2.0	20	15.7	120
	0.25	50	16.5	95
	0.5	50	17.2	95
	1.0	50	0	95
	2.0	50	1.9	95

occurs only under concentrated alkaline conditions. Tests where soda in solid form was added to the lye showed no adsorption of the dye on the surface of the soda particles. Freshly precipitated solid soda from supersaturated solutions, produced by mixing a concentrated soda solution with a concentrated caustic soda solution, has a larger surface, and this explains the increased adsorption of the dye and the dissolved substances in the lye.

Even the addition of only 0.25% H_2O_2 to the soda-containing solutions gave satisfactory results, which were always above those where no soda was present.

Certain parameters influence the flotation behavior of vat dyes:

1. Time of oxidation—Only fully oxidized insoluble vat dyes must be used.
2. Concentration effect—Too much H_2O_2 can reduce the flotation effect by generating an excess of gas, thus creating undesirable eddies. The additional amount of surfactant necessary for optimum flotation depends on the surfactant concentration already present in the lye.
3. Surfactants added—Anion-active and nonionic surfactants are especially useful in the flotation process. Cation-active surfactants used in flotation had a satisfactory purifying effect, but recycling of such lyes in the mills might be difficult (flocculation).
4. Crystallized solid Na_2CO_3—Precipitated soda crystals can bind color particles to a considerable extent. The excellent flotation qualities of the soda crystals mentioned above can only be ascertained if crystallization is carried out immediately before application.

The flotation results with naphthol dyes are given in Fig. 2. The decrease in pigment concentration by flotation was measured against the concentration of a solution treated in the same manner except for the addition of H_2O_2.

The addition of larger quantities of peroxide reduces the concentration of the dyestuff considerably. In the untreated lyes an average dyestuff concentration of 20–60% (maximum 68%) of that theoretically possible was found. Whenever H_2O_2 was added to the lyes, a further decrease of dyestuff concentration was achieved. The effect of the mercerizing auxiliary Mercerol SAW (anionic) was investigated. 0.1 mL Mercerol SAW was added to 25 mL lye. The results, given in Table 5, show no significant improvement of the flotation effect.

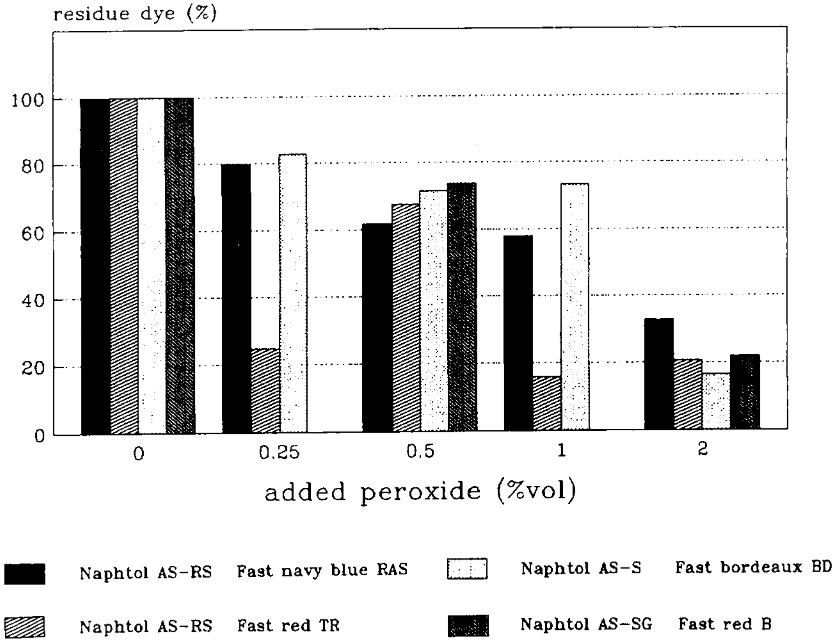

FIG. 2. Flotation of naphthol dyes at various peroxide additions.

TABLE 5
Flotation of Naphthol Dyes with the Addition of Mercerol SAW

Naphthol	Coupling compound	H_2O_2 added (vol%)	Residue dye (%)
AS-RS	Fast navy blue RAS	0	94.8
		0.5	67.8
AS-RS	Fast red TR	0	63.4
		0.5	92.9
AS-S	Fast bordeaux BD	0	74.5
		0.5	39.9
AS-SG	Fast red B	0	86.8
		0.5	48.2

TABLE 6
Flotation of Cotton Dust[a]

H_2O_2 added	Temperature	Recovery (%)
0	RT	13.6
0.25	RT	<5
0.5	RT	<5
1.0	RT	<5
2.0	RT	<5
0	50°C	15.2
0.25	50	9.6
0.5	50	5.5
1.0	50	5.0
2.0	50	<5

[a]Average fiber length, 0.88 mm; duration of experiments, 80 min.

In addition to dye particles (mercerization of colored woven goods), parts of fibers (dust, fiber fragments) are also found in the lyes used in industrial mercerization processes. If dyed fiber particles are in the lye to be recycled, it is even more important to remove all linters. The removal of cotton dust, which served as a model substance for the fiber parts present in industrial lyes, was investigated.

The pertinent results are given in Table 6. Chemical flotation of cotton linters proves to be very satisfactory, as 80–90% of the total cotton dust can be removed without adding other substances. The results show a marked decrease if H_2O_2 is added.

The experiments with model systems showed that a satisfactory removal of impurities is possible. Soda crystals can be totally eliminated. Depending on the flotation parameters, 60–80% of dyes and more than 95% of fiber particles can be removed.

Calculations of costs of an apparatus working on a technical scale show that treatment of reboiled mercerizing lyes with chemical flotation allows amortization in a relatively short time.

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