The Color of Liquid Caustic Soda Produced by the Ammonia-Soda Process

By Hiroshi AWAYA

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Inasmuch as the chromium in an electrolyte has an influence on chlorine-caustic electrolysis in the electrolytic-soda process, small amounts of chromium in the electrolyte and in the products have been measured, but in the ammonia-soda process, the amount of chromium in the products has not yet been measured.

Caustic liquor produced by the ammonia-soda process has a characteristic yellow color. For the present article, the cause of such coloring was studied by polarographic and spectrophotometric methods, and it was found that the coloring was due to a chromate contained as an impurity in the caustic liquor.

Then the chromate content in many steps of the manufacturing process was determined. As a result of this experiment, it was found that the chromate in the caustic liquor comes from the milk of lime used for causticization.

Preliminary Experiments

Polarographic Method.—Caustic liquor samples from both ammonia and electrolytic processes were used. The sample of the ammonia process had a marked tinge of yellow. This sample was diluted with water and tartaric acid was added to make 0.2 M of an acid tartrate solution (pH 4.5). A small quantity of gelatin was also added. The polarograms of these solutions are shown in Fig. 1.

The polarogram of the sample from the ammonia process shows an abnormal wave. This wave seems to be due to a hydrolysis current[1].

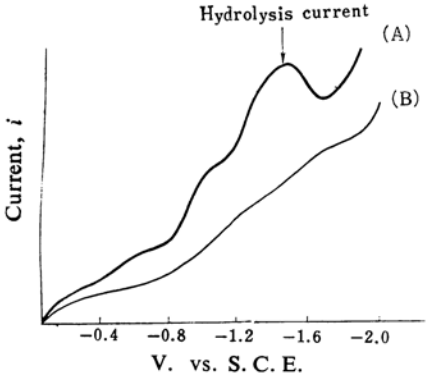

Fig. 1. Polarograms of caustic liquor as 0.2 M acid tartrate (pH=4.5).
(A) Ammonia-soda process
(B) Electrolytic process

Although the polarographic study of chromate ions by Lingane and Kolthoff[2] did not describe this hydrolysis current, and the half-wave potential did not coincide exactly with the values obtained by Lingane for chromate ions[3]; it seems to the author that the existence of chromate in the sample caused this hydrolysis current. This method did not give however, reproducible results. It might be that the coloring was due to the chromate, but this could not be confirmed by the polarographic method.

Absorption Spectra. — If the coloring of the caustic liquor was caused by the chromate contained as an impurity, the absorption spectra of the sample would show an absorption maximum at the wavelength of 370 mμ[4]. Therefore, the absorption spectra of many sorts of caustic soda were determined.

The samples were diluted to a 25% solution, and their absorbancy was determined photometrically over the wavelength range from 340 to 700 mμ. The data obtained are shown in Fig. 2.

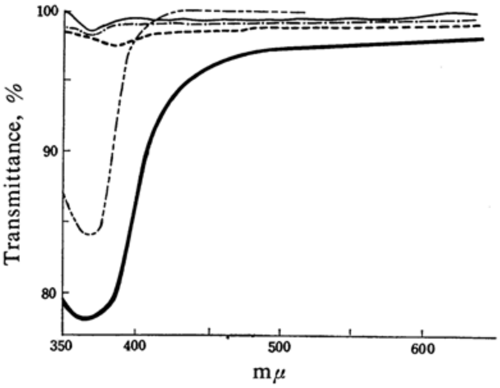

Fig. 2. Absorption spectra of caustic soda. 25% NaOH solution, 1 cm.-glass cell
—— Chemical pure reagent
-·-·- Caustic liquor (electrolytic)
---- Caustic solid (ammonia)
━━ Caustic liquor (ammonia)
·---- Chromate solution (Cr: 2.5 p. p. m.)

The caustic liquor produced by the ammonia

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1) M. Shinagawa, "Polarographic Determination", Kyoritsu Shuppan Co., Tokyo (1950), p. 126.

2) J. J. Lingane and I. M. Kolthoff, *J. Am. Chem. Soc.*, **62**, 852 (1940).

3) J. J. Lingane and R. L. Pecsock, ibid., **71**, 425 (1949).

4) E. B. Sandel, "Colorimetric Determination of Traces of Metals", Interscience Publishers, Inc., New York (1959), p. 390.

process had an absorption maximum at 370 mμ, agreeing with the characteristic absorption band of chromate. When the caustic liquor was concentrated to an anhydrous solid, even if it was produced by the ammonia process, it showed no absorption maximum at 370 mμ. This was due to the addition of sulfur, used as a refining reagent for solid caustic soda.

Experimental and Results

The Determination of Chromium.—As it was established that the coloring of the caustic liquor produced by the ammonia process was caused by chromate, the chromium content at many steps of the caustic manufacturing process was determined[5].

The chromium content in the electrolytic caustic soda was also determined.

Preparation.—Liquid caustic soda (50%): Dilute 50 ml. of the sample with water to about 200 ml.

Sodium carbonate solution: Dilute 100 ml. of the sample with water to about 200 ml.

Salt: Heat 100 g. of the sample with 100 ml. of 1 : 9 hydrochloric acid, add water until dissolution, and filter the solution in order to remove insoluble substance.

Limestone and burned lime: Take 20 g. of limestone and 5 g. of burned lime respectively. Moisten the sample powder with water, add 6 N hydrochloric acid until the bubbles of the carbon dioxide gas disappear, and dilute the mixture with water. Then heat the solution and, after cooling, filter it for removal of the insoluble substance.

Milk of lime: Dilute 10 ml. of the sample with water, and 6 N hydrochloric acid until the bubbles of the carbon dioxide gas disappear, and dilute the mixture with water. Then heat the solution.

Operation of Analysis.—If the sample solution is neutral of alkaline, add hydrochloric acid to the solution until it is acidic (pH 1∼2). If the sample solution is highly acidic, add aqueous ammonia. Heat the solution carefully, add 5 ml. of a ferrous solution (1 mg. Fe^{2+} per mol.) for the reduction of the chromate and, after a while, add 0.5 ml. of concentrated nitric acid in order to oxidize the ferrous ion. Add aqueous ammonia (12 N) excessively to the solution at 30 to 40°C. The precipitates of ferric and chromium hydroxides are filtered and dissolved with 20 ml. of hot mixed acid (10% concentrated sulfuric acid, 10% concentrated phosphoric acid, and 80% water by volume). Dilute to about 40 ml. with water, heat the solution and, keeping it warm, add the potassium permanganate solution (0.5%), drop by drop, until the solution comes to have a tinge of the purple color of the permanganate for 10 min. After cooling, add 10 ml. of a urea solution (10%) and then sodium nitrite solution (10%), drop by drop, until the pink color disappears. Stir the solution vigorously until the bubbles are broken, transfer the solution to a 100 ml. volumetric flask. Add 3 ml. of diphenylcarbazide solution (0.2% alcoholic solution) and then shake it and allow it to settle for a minute. Add 5 ml. of hydrofluoric acid (4%) in order to mask the ferric ion, dilute to 100 ml., determine the absorbancy photometrically at 540 mμ using a blank solution (containing ferric ion and all reagents) as a reference and compare it with the calibration curve.

TABLE I. DETERMINATION OF CHROMIUM ON THE SODA INDUSTRY

Materials			Cr, %
Salt	Egypt-salt		<0.000004
	Aden-salt		<0.000004
	Formosa-salt		<0.000004
	Taku-salt		<0.000004
Brine (electrolytic soda process)			
	Purified brine		0.0000030
	Depleted brine		0.0000045
Limestone			0.00027
Burned lime			0.0025
Milk of lime		No. 1	0.00038
		No. 2	0.00026
Na_2CO_3-solution (before the causticization)			0.00000
Liquid caustic soda (45%)			
	Ammonia process		
		No. 1	0.00019
		No. 2	0.000084
		Maker A	0.000115
		Maker B	0.000133
		Maker C	0.000135
	Electrolytic process		
		No. 1	0.000005
		Maker A	0.000048
Solid caustic soda		No. 1	0.000007
		No. 2	0.000062

The results of the determination of chromium content are shown in Table I.

The chromate was also found in the caustic liquor produced by several ammonia process makers in Japan.

As shown in Table I, the salts used as raw material and the sodium carbonate solution used for causticization contained little chromium. A considerable amount of chromium was found in limestone, burned lime and milk of lime. It was thus confirmed that the chromate in the caustic liquid came from the limestone.

Discoloring of the Yellow Colored Caustic Liquor.—Discoloring of the caustic liquor produced by the ammonia process was attempted.

The caustic liquor samples used were 10% solutions.

Treatment 1.—Add the powder of ferrous sulfate or strontium sulfate up to 1% of the solution, then stir and filter the solution. The chromate in the solution was reduced by this method, precipitated as chromium hydroxide and removed from the solution.

Treatment 2.—Let the sample solution pass through a column of anion exchange resin (Amberlite IRA-410, OH-form). The chromate in the solution was adsorbed in the resin, and the solution was purified. After each treatment, the

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[5] Japanese Industrial Standards, JIS G-1217 (1958).

TABLE II. DISCOLORING OF CAUSTIC LIQUOR

Treatment	Cr, %
Before treatment	0.000034
Addition of excess of $FeSO_4$	0.000012
Addition of excess of $SrSO_4$	0.000014
Treatment with anion exchange resin*	0.000008

* Amberlite IRA-410, OH-form

chromium content of these solutions was determined. These results are shown in Table II.

Yellow colored caustic liquor was discolored by the addition of ferrous sulfate or strontium sulfate.

The application of anion exchange resins was also effective.

Summary

It is found that the coloring of caustic liquor produced by the ammonia-soda process is due to chromate in the milk of lime given to the sodium carbonate solution for causticization. But the solid caustic soda, even produced by the ammonia-soda process, contains a little chromate. The coloring of caustic liquor by chromate is found in products of all ammonia process makers in Japan.

The existence of chromate not only gives the yellow color to the product, but also has an undesirable effect on viscose production in the rayon industry.

Yellow-colored caustic liquor can be discolored by the addition of the reducing reagent. Refining by anion exchange resin is also effective, but there is a risk of the corrosion of the resin by the caustic liquor. As the chromate was identified in the caustic liquor, it was concluded that the abnormal wave of the polarogram caustic liquor was probably due to the hydrolysis current.

By measuring the absorbancy of caustic liquor at the wavelength of 370 mμ, the chromate content can be nearly exactly determined.

As much limestone contains a considerable impurities, it is not desirable to use the milk of lime for the purification of the brine in the electrolytic-soda process also.

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Tokuyama Soda Co., Ltd.
Research Division
Tokuyama