

Pan Scale

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Received for publication March 13, 1968

The term "pan scale," as commonly used for non-sugar particles originating in the vacuum pan and showing up in sediment tests, may be divided into two main categories: 1) Inorganic scale which most often consists of oxides of metals and formed through corrosion of the pan parts and loosened through abrasion by the sugar. 2) Inorganic or organic scale formed by chemical deposition in the pan.

The first category may be largely eliminated by the use of corrosion resistant metals and the use of cleaning fluids or compounds with low corrosive action. It is not necessary to pursue the cause and prevention of this type of scale as the problem is a familiar one.

The second category is still one where causes are not fully known.

The following discussion describes a scaling problem which has been experienced at Spreckels factories and probably at the factories of other sugar companies.

In the late fall of 1959 and spring of 1960 a frequent occurrence of a white scale in sediment tests of sugars at the Woodland factory was noticed. Examination of the sugars at the Spreckels and Manteca factories did not show the presence of this type of scale. The scale was not visible on a white sediment pad, except for careful examination under magnification, but could be readily seen on a black pad due to the size of the thin particles.

The substance had some resemblance to tiny soap flakes having a waxy appearance with the thinnest scales being nearly transparent. Generally the flakes would show laminations suggesting that they were formed intermittently over a period of time. The flakes were readily soluble in dilute hydrochloric acid leaving a slight residue. They would burn leaving a white ash and were insoluble in organic solvents. They were slowly and partly soluble in boiling water. The inorganic constituents varied from time to time, except for calcium which remained at 14 to 16% in analyses of a number of samples.

Other elements would be present in varying quantities, such as silica from 1 to 17% as SiO_2 , iron and aluminum from 1 to

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5%, magnesium from 0 to 1%. Analyses of a number of samples showed varying organic constituents. At this point the compound could be broadly classified as principally a calcium salt of one or more organic acids.

The white scale appeared later in the Spreckels and Manteca factories. However, by this time certain preventative measures had been adopted so that the presence of this type of scale was greatly minimized.

The rather sudden appearance of the white scale prompted us to investigate the possible causes. Changes in beet supply or factory processes were considered.

We came to the conclusion that there had not been drastic changes in such factors as climatic conditions, beet varieties, fertilization, retention time between harvesting and processing, etc. A gradual change from hand harvesting to mechanized harvesting was taking place resulting in an increase in tops and tails.

During the years since the first appearance of the white scale, the factory personnel have observed that a higher incidence occurs at the end of the Fall campaign and the beginning of the Spring campaign. The scale occurred in the "straight" house as well as in the factories using the Steffen process. The formation in the pans was increased with higher pH of the charge.

While a major change in the factory processing had occurred, namely, that of activated carbon treatment of the thick juice, we had occasion to test sugars which were manufactured prior to the installation, and found the presence of the white scale which had formerly not been noticed.

Other steps in factory processing were investigated and no other possible causes for the formation of the scale in the pans were found.

Due to the scale being principally a calcium salt, it is reasonable to assume that by keeping the lime salts low the scale formation would be minimized. When higher lime salts occurred, even though the alkalinity of second carbonation was kept as close as possible to the optimum, we did not find a correlation between higher lime salts and increase in formation of the white scale.

In a number of analyses by wet methods indications were found of the presence of more than one organic acid. One tentatively identified was malic acid. It was also indicated that the organic constituents were probably present in varying amounts at different times.

When the scale first appeared, analytical equipment was not available at the Spreckels laboratories for more precise determinations of the organic constituents. Only recently a sample of scale, which had been removed from the pan tubes during

the time of early appearance of the scale, was analyzed by the Spreckels Research Department.

The analytical scheme consisted of dissolving 0.6 grams of the scale by placing it in water and adjusting the pH to 4 with hydrochloric acid, filtering, and passing the solution first through a cation and then through an anion exchange column. The eluates from the two columns and the neutral effluent were evaporated to dryness and methylated by the method of Gehrke and Stalling. (1)² The fraction from the cation column and the neutral fraction were subjected to analyses by gas chromatography. Only small amounts of organic materials were found.

A gas chromatogram of the fraction from the anion column showed two major peaks. (Figure 1) Retention time data indicated that peak No. 1 was dimethyl malate and that peak No. 2 was trimethyl citrate. The identities were confirmed by comparison of their infrared spectra with known standards. (Figure 2 and Figure 3)

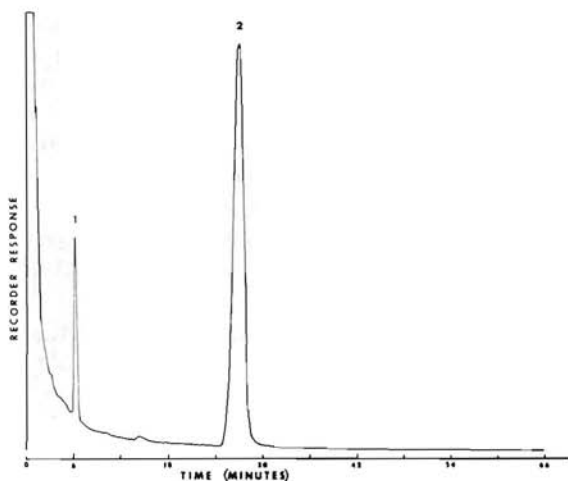


Figure 1.—Chromatogram of the methylated anion exchange column eluate from a sample of pan scale. Column 6' \times $\frac{1}{8}$ " O.D. packed with 20% DEGS on acid washed, silanized 60 - 80 mesh Chromosorb W; oven temperature 180° C; gas flow 40 cc/min.

The quantitative composition of this single sample is estimated to be

	% on solids
Inorganic	50
Citric acid	26
Malic acid	5

² Numbers in parentheses refer to literature cited.

Oxalic acid	}	2
Lactic acid		
Glycolic acid		
Succinic acid		
Not identified		17

It has been found that the natural organic acids present in sugarbeets are largely precipitated and eliminated during carbonation. However, the initial quantity, solubility and possible change in chemical composition may be factors in the amount passing through and precipitating when higher concentrations are reached in the pans.

While we have not found the initial cause or the conditions favoring the carry-through of the organic constituents to the pans, we have adopted certain measures which have greatly minimized the problem. These are: 1) Careful attention to minimizing soluble lime salts by keeping second carbonation alkalinity at the optimum. 2) The use of soda ash when the

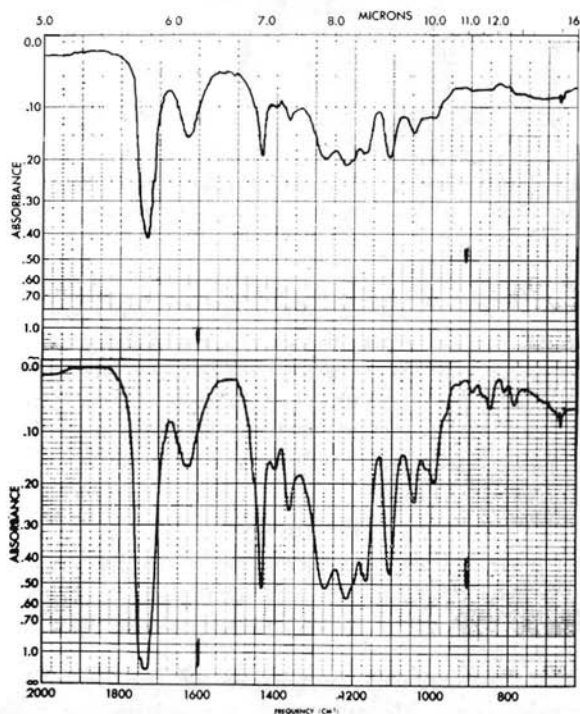


Figure 2.—Top, infrared spectrum of peak No. 1, Fig. 1, trapped on powdered KBr, 13 mm pellet. Bottom, infrared spectrum of 0.4 μl dimethyl malate, 13 mm KBr pellet.

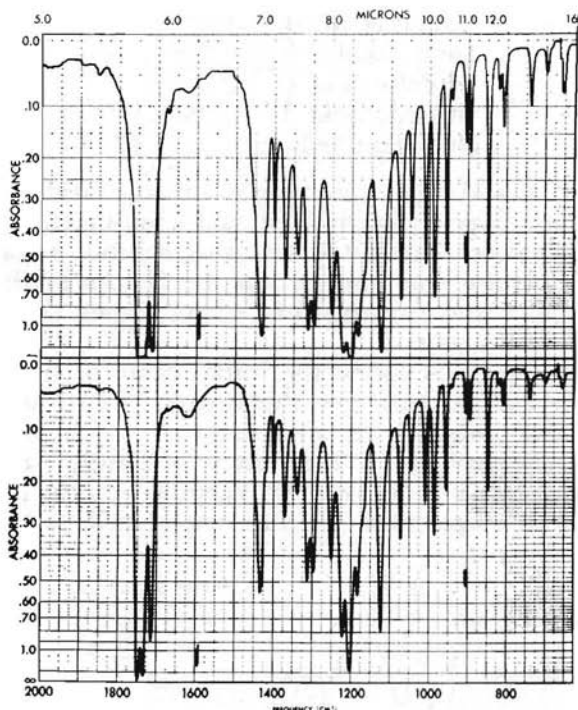


Figure 3.—Top, infrared spectrum of peak No. 2, Fig. 1, trapped on powdered KBr, 13 mm pellet. Bottom, infrared spectrum of $0.5\mu\text{l}$ trimethyl citrate, 13 mm KBr pellet.

first measure is not fully satisfactory. 3) Boil-out of the pan when any sign of the scale shows up on sediment pads, which can be recognized by an experienced analyst when fractions of parts per million are present. For boil-out it is only necessary to use very slightly acidified water. Versene was found to be effective but more costly.

Summary

A white scale which has been occasionally troublesome in pans at the Spreckels factories was identified as calcium salts of organic acids such as citric, malic, oxalic, lactic, glycolic, succinic and possibly others.

The conditions causing formation of the scale in the pans were not established. Measures for preventing or greatly minimizing its presence were adopted. Such measures consist of controlling carbonation at optimum alkalinity, the use of soda ash when necessary, and boil-outs of the pans as necessary.

Acknowledgment

We appreciate and acknowledge the assistance of Gerda Madsen and T. S. Morrill, organic chemist and research assistant, respectively, of the Spreckels Research Department, in identifying the organic constituents of a sample of white pan scale.

Literature Cited

- (1) GEHRKE, C. W. and D. L. STALLING. June 1966. Quantitative Analysis of the Twenty Natural Protein Amino Acids by Gas Liquid Chromatography. Presented at the 19th Annual Summer Symposium, Analytical Chemistry, University of Alberta, Canada.