Inhibitors and Accelerators in Autoxidation of Soaps

II. Inorganic and Organic Chemicals

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SEVERAL chemicals have been mentioned in the literature as active inhibitors in soap autoxidation. In this series 19 chemicals were tested by the same method as described in the first paper, using the direct oxidation test on soaps. Table 1 contains the results of this series of experiments.

The strongest inhibitive action was shown by a- naphthylamine, which however, dyed the soap dark violet-brown almost instantaneously. Second strongest was the effect of hydroquinone (the soap darkened to grey-brown). Third diphenylamine (the soap turned light grey-beige). β-naphthol dyed the soap in the same manner as diphenylamine while thymol and carvacrol had only a slight effect on its color.

Sodium thiosulfate, very often mentioned as an antioxidant, kept the peroxide value down for 70 hours, but it cannot be proved at present whether this was a direct effect on oxidation, or probably a mere secondary effect, through reduction of the iodine developing during the peroxide value test. At any rate, this action broke down suddenly after 70 hours, and peroxide value was subsequently developing rapidly.

A very remarkable fact is that flowers of sulfur showed a distinct inhibitive action, especially during the initial stage. The well known reducing agents, sodium hydrosulfite and sodium bisulfite, did not give any protection. Magnesium silicofluoride has proved to be an energetic accelerator.

Action of Metals. Substantial work has been done on this subject, but the reliability of the results of previous work appears doubtful because of the lack of suitable methods for control.

Adolph Grün carried out experiments with traces of various metals in soaps, the means of control in this case having been observation of the degree of darkening. The result of these experiments were later published by F. Wittka (1), who stated that there exists an "activity series" as follows, according to the extent of darkening:

$$Cu > Co > Fe > Ni > Mn > Hg > Pb > Sn$$
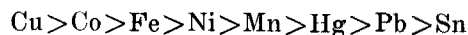
The darkening effect was then, and has been until now, regarded as an appropriate measure of the oxidation-accelerating properties of the metal.

Experimental. The same normal soap-base flakes as mentioned in the first paper were milled with amounts of metal salts corresponding to 0.025% metal in the soap. The metal salt was added dissolved in distilled water corresponding to 4% of the soap. The soap flakes have no peroxide value at the outset. Exposure was carried out, during day and night, as described in the first paper. The results are reported in Table 2.

It can be seen that cobalt had a truly "explosive" influence. Copper, though also very active, lagged considerably behind. The experiments were started at noon, and by next morning both cobalt and copper samples were found to have developed an intensive rancid smell.

All other metals were practically inactive during the first period of about 96 hours, although iron, in both its forms, did give some results on the first day. However, when the acid value of the samples after 140, 332, and 760 hours are taken into consideration, it can be seen that besides cobalt and copper, manganese, chromium, and iron also had some effect on the soap although the peroxide values did not show any significant differences to the uncontaminated soap.

According to these experiments, the "activity series" of metals in rancidification of soap should be as follows:

$$Co > Cu > Fe > Cr > Mn$$
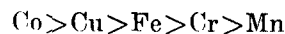
instead of Wittka's series as mentioned above. There was a change of color in the soaps with manganese

TABLE 1

Chemical (1%)	Peroxide value after (hours)								Acid value or free NaOH
	22	48	70	110	168	216	336	840	840
None*	7.0	16	21.5	44	51	54	76	105	2.4 A.V.
Sodium bisulfite	8.0	15	23	50	58	72	104	115	9.0 A.V.
Sodium hydrosulfite	3.5	10	16	39	46	54	78	105	7.4 A.V.
Magnesium silicofluoride	8.5	23	31	88	106	106	120	110	18.0 A.V.
Flowers of sulfur	2.2	7	8.5	18	24	29	45	85	9.0 A.V.
Sodium thiosulfate	0.0	0.0	0.0	12	20	28	42	95	2.6 A.V.
Diethylaniline	3.0	8.5	16	36	42	55	84	125	2.4 A.V.
Paraldehyde	9.5	18	23.5	50	50	67	80	110	3.4 A.V.
Naphthoquinone	3.0	7.0	8	30	36	48	78	110	3.4 A.V.
α-Naphthylamine	0.0	0.0	0.0	0.0	2.0	2.0	2.0	2.0	0.4 A.V.
Salicylic acid	7.0	12	17	34	42	46	58	95	2.0 A.V.
β-Naphthol	3.3	6.0	8.5	14	20	24	29	70	0.6 A.V.
Hydroquinone	1.0	3.0	3.0	4.0	4.0	4.0	6.0	17	4.0 A.V.
Diphenylamine	1.0	2.2	3.0	7.0	7.4	10	11	22	0.015% N.OH
Citric acid (natural)	7.5	15.5	22	43	52	58	81	120	7.6 A.V.
Thymol	3.5	6.0	9	18	26	25	37	75	0.03% NaOH
Carvacrol	4.5	8.5	10	20.5	26	30	39	85	0.03% NaOH
Hexamina	8.0	13.0	20.5	42	42	52	68	100	1.2 A.V.
Paraformaldehyde	8.0	11.5	17	37	44	48	72	115	2.0 A.V.
Waterglass ($Na_2O:2SiO_2$)	7.5	12.5	19.5	38	45	48	50	95	0.04% NaOH

* Initial P. V. O. 0.

TABLE 2

Metal	Salt used	Peroxide value after (hours)								Acid value or % free NaOH after (hours)		
		20	68	96	120	192	260	332	760	140	332	760
None*		5.0	16	19.5	29	40	48	70	112	0.02 NaOH	0.02 NaOH	2.2 A.V.
Manganese (bivalent)	Chloride	5.0	19	19.5	24	35	46	59R	85	0.4 A.V.	2.8 A.V.	4.6 A.V.
Chromium (trivalent)	Chloride	5.0	15.5	22.5	29	40	49	69R	95	Neutral	1.8 A.V.	5.6 A.V.
Copper (bivalent)	Sulfate	28 R	49	39.5	46	50	50	58	85	5.6 A.V.	6.8 A.V.	10.0 A.V.
Zinc	Sulfate	4.5	15	20	34	50	59	75	120	0.02 NaOH	0.02 NaOH	2.8 A.V.
Tin (bivalent)	Chloride	4.5	11	17	32	45	64	68	110	0.02 NaOH	0.02 NaOH	2.2 A.V.
Mercury (bivalent)	Chloride	5.5	15	24	38	45	57	71	125	0.02 NaOH	0.02 NaOH	3.0 A.V.
Lead (bivalent)	Nitrate	6.0	14.5	22	34	45	60	74	125	0.01 NaOH	0.01 NaOH	2.4 A.V.
Iron (bivalent)	Sulfate	7.0	14.0	19	31	40	57	71	100	Neutral	1.0 A.V.	6.8 A.V.
Iron (trivalent)	Chloride	10.5	13.5	18.5	26	35	44	57	82	Neutral	1.2 A.V.	6.0 A.V.
Nickel	Sulfate	5.5	13.0	20	26	32	50	58	100	0.01 NaOH	Neutral	2.6 A.V.
Cobalt	Sulfate	65 RR	65	68	77	85	86	93	120	8.6 A.V.	12.6 A.V.	16.4 A.V.

R—Rancid odor beginning to develop.
RR—Strongly rancid odor beginning to develop.
* Initial P.V. 0.0; Free NaOH 0.03%.

and iron (both forms), but it should rather be attributed to the natural colors of the corresponding metal soaps.

In order to obtain a more comprehensive picture of the effect of cobalt and copper, additional experiments were carried out, in which samples with cobalt and copper were again compared to a blank (uncontaminated) sample. In this additional series, the first peroxide value was determined 2 hours after the soap had been milled with the metal salts. Results in Table 3.

In this series we observed that during the initial stage there was no marked difference between the contaminated and uncontaminated samples. Difference was first observed after 4½ hours' exposure when the peroxide value of the cobalt sample rose to 9, and a distinct rancid odor could be noticed. After 4½ hours covers were placed over the boxes, and after 18 hours in the dark, the cobalt sample (P.V. 68) was well ahead of the copper sample, which already had a rancid smell (with P.V. 10). After 22½ hours' exposure to light, plus 4 x 18 hours in the dark, uncontaminated soap was not yet rancid at all, a fact corroborated by the unchanged acid value. Here again the cobalt sample had a much higher acid value than the copper sample.

In a third series of experiments the same samples were kept for 72 hours in the dark. Results in Table 4.

TABLE 4

Metal	Peroxide value after 72 hours in the dark	Acid value or free NaOH
None	0.7	0.03 NaOH
Copper 0.025%	29 R	1.4 A.V.
Cobalt 0.025%	70 RR	6.0 A.V.

The effect of metal accelerators in the dark seems to be even more marked. Uncontaminated soap remained almost unchanged after 72 hours, whereas the cobalt and copper samples had accumulated a substantial amount of peroxides. Metal accelerators are, accordingly, active even without the effect of light.

Organoleptic Rancidity and the Peroxide Value. It was already shown by various workers that inhibitors in peroxide development in oils are not only able to slow down the development of peroxides, but in certain cases they also raise the level of peroxide accumulation at which rancid odor can be observed.

In our own series of experiments with metal accelerators we could, on the contrary, observe that, in the presence of the active metal accelerators, organoleptic rancidity appeared already at a much lower level (P.V. 9) than in the case of uncontaminated soap.

It will be remembered that peroxide values in oils do not rise indefinitely, but the curve shows a maximum, after which it declines. This diminishing of the peroxide value must be explained as a decomposition of accumulated peroxides. It is obvious that from a certain stage, accumulation and decomposition proceed simultaneously, the final result depending on the relative velocities of both.

It is accordingly quite possible that, in the case of metal-contaminated soaps, the first peroxide value at which rancid odor was observed was already a result of such a simultaneous process, decomposition of peroxides probably proceeding faster than their formation in the presence of metal contaminants, which can be seen at a later stage, by comparing A.V. with P.V.

Summary

1) Nineteen organic and inorganic chemicals were tested for their action in peroxide accumulation in soaps.

2) The effect of small quantities of various metals in soap was tested, and a new "activity series" was proposed.

3) The relative effect of metals in accelerating peroxide formation is more marked in the dark than in light.

4) In the presence of metallic accelerators, organoleptic rancidity appears at a much lower peroxide value than in the case of soap uncontaminated by metals.

REFERENCE

1) F. Wittka, Seifensieder—Ztg. 54, 74o (1927).

TABLE 3

Metal	Peroxide value after (hours total). Each period includes the previous periods.										Acid value or free NaOH 22½ᵇL +72ᵇD
	2L	4½L	18D	8L	10½L	36D	17½L	54D	22½L	72D	
None	5.5	6.6	7.0	14	17.5	18	28.5	33	44	44	0.015NaOH
Copper 0.025%	4.8	6.0	10 R	17.5	20	34	39	46RR	60	58	3.6 A.V.
Cobalt 0.025%	5.8	9.0R	68 RR	80	87	92	95	102	104	102	10.6 A.V.

L—In daylight. D—In dark. R—Rancid odor beginning to develop. RR—Strongly rancid odor.