

# Inhibitors and Accelerators in Autoxidation of Soap

## I. Soap Perfuming Chemicals

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THE chemical processes preceding or following the spoilage of soaps have not been studied in the exact manner as is the case with oils. It is natural, therefore, that a number of problems concerning the deterioration of soaps are still unsolved while investigations on pure oils are far more advanced. In dealing with rancidity in oils, the generally accepted method was to follow the progress of autoxidation by direct measurement of the oxygen absorbed, or by a determination of the peroxides accumulated, while testing the oil organoleptically at the same time.

Rancidity in soaps has hitherto been tested almost exclusively by organoleptic methods. Thus, a piece of soap showing some discoloration, or some change in odor was regarded as having become rancid. A great deal of controversy arose, for instance, over the question whether or not various aromatic chemicals played the roles of accelerators or inhibitors in soap deterioration. Thus, in a paper on "Judging Soap Antioxidants by Discoloration" (1), discoloration was again considered as a measure for rancidity, but on the other hand it was considered possible that discoloration might be caused by inhibitors themselves; eugenol was mentioned in this connection.

It is known that compounds of the eugenol group cause more or less immediate discoloration when milled into soaps, and their role in soap perfuming has been widely discussed. One of us, writing on this subject several years ago (2) advanced the opinion that these aromatic chemicals might have a pro- or anti-oxidative influence on the soap-body. In order to learn more about this subject it was proposed to study the behavior of these chemicals in vegetable oils, for which the method of determination of the peroxide value was already in full use at that time.

A review of experiments (3) in the course of which 30 aromatic chemicals were tested for their influence on the autoxidation of linseed oil was quoted in order to draw a comparison with what might happen if

the same chemicals were added to soaps. It must be understood that at that time no direct quantitative method for following autoxidation in soaps was known, and the drawing of a parallel to what has been established for oils was of certain interest, but it was never assumed that the results obtained for oils would necessarily be valid for soaps as well. For details, we would refer to the literature of that time (4, 5).

The following were the tentative conclusions from the study of these experiments, as quoted in *Soap*:

"Aldehydes of the fatty series and of the terpene series act as relatively weak accelerants while aromatic aldehydes have a very strong action. This affords a new explanation of the harmful action of aldehydic perfumes on soap. The aromatic acids, in which the carboxyl group is directly joined to benzene ring, are slightly accelerating, while those in which the carboxyl group is present in the side chain are inactive. The injurious action of acid-reacting perfumes, manifested on the neutralization of the free alkalis of the soap by the carboxylic acid group, may be accelerated in many instances because of the property of these acids to promote oxidation.

"Aromatic ketones are strong oxidation promoters in contradistinction to aromatic terpene ketones. The aromatic ketones must not be used in perfuming soaps. Aromatic terpene hydrocarbons, aromatic unsaturated alcohols of the terpene series and aromatic alcohols appear to be either slightly accelerating or inactive. Esters of the monovalent phenols are strong oxidation promoters. On the other hand the derivatives of the multivalent phenols, which contain hydroxyl groups as well as ethyl-ether, propenyl, and ethyl groups, are strong retarders of oxidation.

"The results, obtained with the compounds of the eugenol group, contradict those obtained in practice. It has been claimed that soaps, perfumed with these aromatic chemicals, will discolor and suffer other injury. The results obtained with vanillin and piperonal, which were found to be strong accelerators of oxidation, agree well with practical experience."

### Experimental

The method of direct oxidation tests in soaps (5) gave the means for following the process actually taking place when soaps are autoxidized. In order to decide whether certain aromatic chemicals act as accel-

TABLE 1

Chemical*	Peroxide value after (hrs.)									Acid value or free NaOH after 300 hours	Remarks
	20	42	66	136	184	232	280	350	685		
Methyl-anthranilate.....	8.0	7.0	7.5	12	22	24	34	41	70	NaOH 0.02	Darkened****
Anethol.....	7.5	10	13	25	55	72	74	102	140	NaOH 0.015	
Anisaldehyde.....	7.5	20	24	46	59	56	88	100	145	0.0	0.0
Bromostyrene.....	8.0	16	20	24	55	75	84	110	123	0.0	
Nitrobenzene.....	6.0	11	16	27	60	82	82	104	145	0.0	0.0
Benzylbenzoate.....	7.5	22.5	24	54	54	66	76	100	140	NaOH 0.015	
Benzaldehyde.....	7.5	14	23	26	60	54	75	86	115	NaOH 0.01	0.0
Cinnamic-aldehyde.....	5.5	7.5	13	65	44	50	74	108	150	A. V. 0.6	
Citronellol.....	8.5	21	23.5	32	55	66	78	88	120	NaOH 0.03	0.0
Phenyl-ethyl alcohol.....	9.5	17	30.5	35	56	67	88	98	120	NaOH 0.015	
Ionone.....	6.5	16	22	38	53	61	72	100	132	NaOH 0.025	0.0
Eugenol.....	2.5	5.0	5.0	11	13	18	26	33	69	NaOH 0.03	
Benzyl alcohol.....	10.0	14	19.5	58	54	76	69	116	150	0.0	Darkened+++
Citral.....	9.0	15	22	35	52	63	74	115	140	A. V. 0.2	
Nerol.....	10.0	32	27	40	62	68	98	92	132	NaOH 0.025	0.0
Vanillin.....	1.5	4.0	4.0	4.0	7.0	10	12	17	32	A. V. 1.4	
Haliotropin.....	5.5	13.5	17.5	22	44	49	65	69	130	A. V. 0.2	Darkened++++
Coumarin.....	4.0	6.0	7.8	17	27	30	37	61	110	NaOH 0.03	
Borneol.....	9.5	21.5	22	50	63	78	80	124	145	0.0	Darkened++
Pure soap (Initial P. V. 0.0).....	8.0	17.5	24	48	71	85	94	128	160	0.0	

\* Supplied by courtesy of the Palestine Frutarom Ltd., Haifa Bay.

TABLE 2

Time (hours)	Pure soap	Coumarin		Methyl-anthranilate		Vanillin		Eugenol	
		0.5%	0.1%	darkened		sl. dark-ened	0.1%	0.5%	0.1%
				0.5%	0.1%	0.5%			
		sl. dark-ened							
22.....	9.0	4.5	7.0	3.5	5.5	1.5	2.5	3.5	7.5
46.....	15	8.5	13.5	6.5	7.5	4.0	5.0	4.3	9.0
70.....	22	11	16.5	11	14.7	4.0	6.8	13.0	20.5
94.....	29	22	28	19	21	5.8	14.0	14.0	23.5

erators or inhibitors, 19 aromatic chemicals, among them some representatives of the eugenol group, were milled into a normal neutral toilet-soap base, based on tallow, vegetable oils, and coconut oil, with an iodine value of 59 of the mixed fatty acids. They were all present in 1% concentration and were added dissolved 1:1.5 in alcohol.

The perfumed soaps were powdered and exposed to normal light and air conditions day and night, and peroxide values determined at intervals, the contents of the sample boxes (30 gms. powdered soap spread on a surface of 18 x 8½ cms.) being well mixed before each test.

Table 1 contains the results of these tests. The first and most obvious observation was that vanillin, methyl-anthranilate, eugenol, coumarin, and heliotropin almost immediately changed the color of the soap, the intensity of darkening being strongest in the case of vanillin and dropping in the respective order to a very slight darkening in the case of heliotropin. Formerly, these aromatics would probably have been considered as causing rancidity in the soap. Now, however, it seems established that these chemicals are the most pronounced inhibitors against autoxidation in soaps so far tested, at least in the concentrations used in these experiments.

The peroxide figures in Table 2 show the effectiveness of four of the above inhibitors in concentrations of 0.5% and 0.1%. It can be seen that vanillin alone has a marked effect as an inhibitor at the concentration of 0.1% while eugenol also shows some activity at 0.5%.

TABLE 3

Time (Hours)	Pure oil	1% Eugenol	1% Vanillin	1% Coumarin
0.....	2.1	2.7	3.0	2.0
20.....	4.5	4.7	4.8	4.5
45.....	7.7	7.2	11.2	7.7
68.....	9.0	9.5	12.6	10.5
110.....	12.7	12.5	24	13.2
182.....	21.5	20.5	42	25.5

### The Behavior of the Inhibitors in Oil

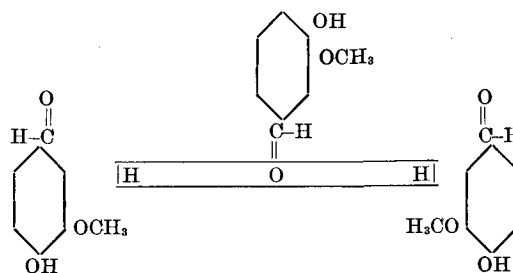
Table 3 shows the autoxidation of oil in the presence of 0.1% vanillin, eugenol, and coumarin, respectively, under the same conditions of light and air as for the soaps. In these experiments 25 grams of oil were kept in 50-ml. beakers. The oil used was refined peanut oil. The solutions were prepared by heating the oil with the added chemicals to 80° C., after which treatment the pure oil had a peroxide value of 2.1.

It can be seen that in oil, vanillin acts as an accelerator whereas eugenol and coumarin are practically inactive. Thus the findings published in 1932 in regard to the pro-oxidative behavior of vanillin in oils were corroborated while it could not be found that eugenol retards autoxidation of oils to any extent. In any case it is now established that an aromatic chemical, in this case vanillin, can behave in

two completely opposite ways when used in two different media such as oil and soap.

*Vanillin.* Vanillin has a hydroxy and a methoxy group attached directly to the aromatic ring in ortho position. Without its aldehyde group, which is in para position to one of the oxy groups, it would have been active as an inhibitor in oils, whereas it has been found to be an accelerator.

As to the possible reason for the inhibitive activity of vanillin in soaps, we would put forward the following hypothesis:

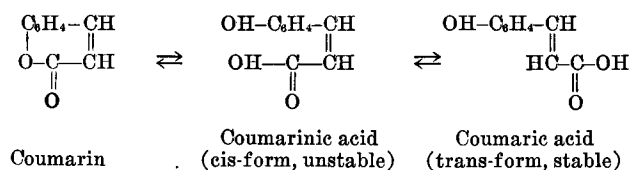


According to this scheme, the aldehyde group of one vanillin molecule is eliminated by binding two other molecules similarly to the model reaction between phenol and formaldehyde. It is likely that the aldehyde groups of the other molecules of vanillin are also eliminated in the same way, thus forming a condensate in which more oxy groups are present in relation to the aldehyde groups than in uncondensed vanillin (6 to 2 in the first stage of condensation, as to 2 to 1 in vanillin itself). It is well known that such reactions are catalyzed in alkaline media, and the intense darkening of the soap is reminiscent of the dark products of condensed aldehydes. According to what is known about the chemical constitution of inhibitors for oils, it seems quite possible that the increase of the number of oxy groups in ortho position (during enlarging of the molecules), at the expense of the aldehyde groups, increases the inhibitive action of molecule as well. As to its accelerating effect in oils, its cause may be the fact that the aldehyde group does not polymerize in oils, thus acting as a pro-oxidative agent.

*Eugenol.* Eugenol contains exactly the same oxy-group as vanillin, but instead of the aldehyde group in para-position it contains an unsaturated side-chain. It darkens the soap to a far smaller extent than vanillin, showing that no condensation reactions are taking place to the same extent as with vanillin. Accordingly, the inhibitive action is also less marked.

In oils, eugenol is inactive, probably on account of the fact that the oxy groups are held in equilibrium by the unsaturated side-chain.

*Coumarin.* It is obvious that, having as it does no oxy group, coumarin cannot be an active inhibitor as such. It is however known that a state of equilibrium exists according to the following scheme:



For the purpose of our investigation it is interesting that coumaric acid shows fluorescence under a quartz-lamp. On the other hand it has been mentioned that maleic acid, incidentally a cis-compound, has the properties of an inhibitor in autoxidation. At the present stage, the explanation seems to be that coumarin is converted, in the presence of an alkali, into the salt of the coumaric acid, which is in turn converted into the stable coumaric form, and it is one of the two salts which acts as an inhibitor.

*Heliotropin* acts somewhat slowly, and it seems that its action is similar to that of vanillin, being slower probably because its two oxy groups are closed together.

*Methylantranilate* seems to act as an aminic inhibitor.

The acid values or free alkali contents (as % NaOH) in Table 1 have been determined after 300 hours of exposure, and it will be seen that most of the strongly oxidized soaps were either neutral or even slightly alkaline. A few of them developed a slight acidity. On the other hand, the soaps whose oxidation was inhibited also varied in their reaction. Thus, the soap with vanillin had a relatively high acid value (caused by the acidity of the vanillin itself) while the ones with eugenol, coumarin, and methyl anthranilate still retained some free alkali.

These series of experiments show again quite clearly that there is no need to suppose that a prior splitting-

off of free fatty acid is necessary for the development of autoxidation and rancidity. The fact that soap oxidizes as such has been proved even more convincingly through an experiment where soap with 8% free alkali has been found to contain very high peroxide values (6).

#### Combination of Vanillin with Other Aromatics

It is probably worth mentioning, in connection with the above experiments, that in the perfuming practice combinations of vanillin with other aromatics have been tried in soaps (7) with the intention of avoiding the darkening effect. It is to be seen how such combinations behave in soaps in regard to their inhibitive action.

#### Summary

- 1) Nineteen aromatic chemicals have been tested for their influence as inhibitors or accelerators in soaps.
- 2) Three compounds of the eugenol group, and one amino-compound have been found to be active inhibitors.
- 3) Their activity was found to be in direct proportion to their darkening effect on soap.
- 4) Vanillin is an inhibitor in soaps and an accelerator in oils.
- 5) Constitutional explanations for the activity of the above inhibitors are put forward.

#### REFERENCES

- 1) Anon., *The Givaudanian*, March, 1941.
- 2) E. J. Better, *Chemiker-Zeitung* 46, 549-560 (1932).
- 3) Tanaka and Nakamura, *Journal of the Society of Chemical Industries of Japan*, 1932, Supp. No. 2, 81B.
- 4) Soap 8, Sept., pp. 59-60 (1932).  
Soap 8, Oct., p. 53, Eric C. Kunz.
- 5) E. J. Better, *Seifensieder Ztg.* 59, 235-238 (1932).
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- 7) O. Gerhardt, *Seifensieder Ztg.* 58, 467 (1931).

## Report of the Cellulose Yield Committee for 1945-46

DURING the past year the committee's work was divided into two parts. Part one was routine checking of yield analyses from different laboratories. Part two was improvements in the method.

#### PART 1

During the year five samples were sent out to eleven laboratories. In some cases all the analyses were not returned so only the laboratories included in this report are the ones which returned the five sets of analyses. These are given in the following table:

Lab. No.	No. sets samples tested	Samples			Over-all average for year
		A	B	C	
		Linters	Linters	Fiber	
1.....	5	77.3	74.3	71.1	74.2
2.....	5	77.8	74.6	70.9	74.4
3.....	5	76.9	73.7	70.1	73.6
5.....	5	77.1	74.2	71.4	74.2
6.....	5	77.3	73.8	70.5	73.9
9.....	5	77.7	74.6	71.3	74.5
10.....	5	77.9	74.6	71.4	74.6
11.....	5	77.6	74.6	71.0	74.4
12.....	5	77.6	74.2	70.7	74.2
Average.....		77.5	74.3	70.9	74.2

It is noted from the above table that the results are fairly consistent and within the experimental error of the method.

#### PART 2

*Improvement 1*—It was suggested that we add a wetting agent to the caustic in order to get a more uniform wetting of the lint before digesting. In order to determine the effect on the yields of this step, three lint samples were sent out to the members of the committee along with the sample of red oil to be used as a wetting agent. The following table gives the yields of the lint with and without the red oil in digesting.

Lab. No.	A		B		C	
	Red Oil	No Red Oil	Red Oil	No Red Oil	Red Oil	No Red Oil
1.....	77.7	77.9	73.2	73.2	72.6	72.2
2*.....	....	....	74.6	74.7	73.4	72.6
3.....	77.6	78.1	73.4	73.5	72.1	72.3
4.....	77.3	77.3	72.2	72.3	71.8	71.6
5.....	78.6	79.0	73.5	73.5	73.2	73.5
6.....	78.6	78.6	74.4	74.1	72.3	72.4
Average.....	78.0	78.2	73.3	73.3	72.4	72.4

\* Poor results due to other reasons than wetting agent. This laboratory is not included in the average.