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Researches on Cellulose Acetate and its Solution. III.

Stabilizer for Cellulose Acetate.

By

Yoshio TANAKA, *Kogakuhakusi*,
Member of the Institute
and
Katsumoto ATSUKI, *Kogakuhakusi*.

Abstract.

Calcium naphthenate is found to be the most effective stabilizer for cellulose acetate as well as for cellulose nitrate. Calcium naphthenate exerts no adverse action on cellulose acetate, and combines with sulphuric acid, present in cellulose acetate, forming calcium sulphate and naphthenic acid. Naphthenic acid produced exerts also no saponifying action on cellulose acetate, and improves the mechanical properties of the cellulose acetate film. Calcium naphthenate and naphthenic acid are the plastizer for cellulose acetate. The amount of calcium naphthenate to be added must be calculated from the amount of the sulphuric acid present, but in general cases 1-2 percent on cellulose acetate will be sufficient.

1. Introduction.

The cellulose acetate, produced as a syrup by the ordinary manufacturing process, using sulphuric acid as catalyst, is precipitated on pouring the syrup into water under agitation, and the precipitate is collected on a filter cloth, and put in a beater. It is first washed with water and then with 2% sodium carbonate

solution under pulping. By this process, the free acid is nearly neutralized and the gel structure of the precipitate is loosened and disintegrated by the evolution of carbonic acid gas. Then the precipitate is again washed with water containing about 0.05% of calcium hydroxide several times, and then with water thoroughly, until the free acid is eliminated.

It is however often found that the cellulose acetate, which is considered to have been purified thoroughly by the above washing, still contains the sulphuric acid residue, present as the ester of cellulose, since the cellulose acetate liberates sulphuric acid on digesting with water at an elevated temperature of 125-130°C under a pressure of 3-5 atmospheres in an autoclave. It is therefore to be considered that the purification is only complete when the cellulose acetate is subjected to boiling. According to the experiments of the present authors, however, the boiling results in the degradation of the chemical and colloidal natures of cellulose acetate.

It is therefore of very importance to stabilize the cellulose acetate by the addition of some substances. In this report the experimental results and discussion of some stabilizers are reported.

2. Experimental.

It is theoretically considered that alkaline substances are effective as the stabilizer for cellulose acetate. But the strong alkalies, such as the hydroxides of sodium, potassium or calcium, or even the weak alkalies such as urea and many amines, can not be used, because the cellulose acetate, which is very sensible to alkalies, is saponified by the alkalies before they are consumed. The stabilizer must exert no adverse action chemically or colloidally on cellulose acetate, and combine with the sulphuric acid, present as ester, or liberated spontaneously in later, forming

a harmless compound. It is considered therefore that the substances, which are neutral but combine with sulphuric acid producing inert substances, are to be used as the stabilizer. Moreover, the stabilizer must be soluble in the cellulose acetate solution, and is desirable to be the solvent or plastizer of cellulose acetate.

After theoretical considerations and experiments, the present authors came to the conclusion that the metallic salts of higher organic acids such as fatty acids or naphthenic acids are most effective as the stabilizer not only for cellulose acetate but also for cellulose nitrate.

The calcium naphthenate used in the experiments was prepared by Yoshio Tanaka[1] from the naphthenic acid, isolated from the petroleum fraction, and was the mixture of calcium salts of tridecanaphthenate $C_{12}H_{23}COOH$, tetradecanaphthenate $C_{13}H_{25}COOH$, pentadecanaphthenate $C_{14}H_{27}COOH$.

Experiment 1. Stabilizing effect of calcium naphthenate.

Cellulose acetate was dissolved in acetone, making a solution of 8 g of cellulose acetete in 100 cc of acetone. The solution was added with 0.08 g of calcium naphthenate, and this solution as well as an another cellulose acetate solution without addition of calcium naphthenate were poured on a glass plate, and evaporated to dryness. The films obtained were cut into small pieces and subjected to the stability tests.

(1) Y. Tanaka, Journal of Faculty of Engineering, Tokyo Imperial University, **13**, 41, 55, 1923; **15**, 271, 1924; **16**, 1, 11, 1924; **16**, 171, 1925; **16**, 183, 1926.

TABLE I.

Sample No.	Properties of Cellulose Acetate					Calcium Naphthenate added %	Stability Tests		
	Acetylation degree CH_3COOH%	Viscosity	Free acetic acid %	Total H_2SO_4 %	Copper number		100°C Test	Decomposition Temperature C	CH_3COOH evolution %
3	55.0	16.0	0.017	0.110	2.8	0 1	70 140	196 212	1.20 0.28
7	55.1	9.6	0.020	0.164	3.2	0 1	65 150	177 202	3.21 0.24
14	57.0	5.2	0.022	0.126	4.2	0 1	60 160	170 198	3.18 1.08
15	57.7	1.7	0.053	0.210	7.6	0 1	30 140	162 196	4.11 1.12
F_2 216	51.2	6.8	0.034	0.114	3.4	0 1	20 180	155 187	4.82 0.76
4	57.0	2.8	0.067	0.568	—	0 1	0 150	101 188	8.20 1.00

The acid vapours, evolved in the acetic acid evolution test, consisted of acetic and naphthenic acid. The determination of acetic acid in the mixture was carried out by using methylorange as the indicator, since the naphthenic acid does not change the colour of that indicator.

From Table 1, it is clearly observed that the cellulose acetate, stabilized by washing thoroughly, gives nearly the same stability tests with or without the addition of calcium naphthenate, but the cellulose acetate, which is unstable owing to the incomplete purification, improves its stability distinctly with the addition of calcium naphthenate.

Cellulose nitrate is also stabilized by the addition of the calcium naphthenate. The comparison of the stabilizing effects of urea, calcium lactate and calcium naphthenate is shown in Table 2.

TABLE 2

	Abel heat test min. at 80°C.			Ignition point, °C		
	1	2	3	1	2	3
Film with no stabilizer	—	90	4.7	174	182	130
Film with 1% urea	—	13	9	172.5	181	168
Film with 3% urea	—	50	6	173.5	176	168.5
Film with 6% urea	—	14.2	13.5	173	170	169.5
Film with 1% Ca-lactate	—	50	8.5	175.2	175	165
Film with 3% Ca-lactate	—	90	3.2	170.5	170.5	172
Film with 6% Ca-lactate	—	120	9	166	166	169
Film with 1% Ca-naphthenate	—	—	—	179	188	179
Film with 3% Ca-naphthenate	—	—	—	182	182	182
Film with 6% Ca-naphthenate	—	—	—	176	184	177

Table 2 suggests that the stabilizing effect of calcium naphthenate is superior to urea and calcium lactate, when applied to cellulose nitrate.

Experiment 2. The effect of naphthenic acid and calcium naphthenate upon the mechanical properties of cellulose acetate film.

The various amounts of naphthenic acid or calcium naphthenate were added to the cellulose acetate solution, made up by dissolving 8 g of the cellulose acetate in 100 cc of acetone. 30 cc of the solution were poured into a definite glass case, and evaporated into a film under a reduced pressure. The film obtained was cut into a strip and subjected to the Schopper testing machine.

TABLE 3

Test No.	Naphthenic acid added. % on cellulose acetate	Tensile strength kg/mm²	Elongation %
1	0	7.2	6.4
2	1	9.4	12.4
3	2	9.0	12.6
4	3	8.6	12.0
5	4	8.0	11.0
6	6	7.3	9.2
7	8	6.4	7.4
8	10	5.3	5.8
Test No.	Calcium naphthenate added. % on cellulose acetate	Tensile strength kg/mm²	Elongation %
9	0	7.2	9.4
10	1	8.4	11.8
11	2	8.0	13.4
12	3	7.6	12.0
13	4	7.7	10.5
14	6	6.0	7.6
15	8	5.6	6.4
16	10	4.2	5.8

3. Discussion.

From the experiment 1 it is clearly observed that calcium naphthenate is the most effective stabilizer not only for cellulose acetate but also for cellulose nitrate.

Calcium naphthenate reacts with the acids present in cellulose esters as

$$H_2SO_4 + Ca\text{-naphthenate} = CaSO_4 + \text{Naphthenic acid}$$

$$2CH_3COOH + Ca\text{-naphthenate} = Ca(CH_3COO)_2 + \text{Naphthenic acid}$$

Thus sulphuric acid, which is the main cause of the instability, is converted into the neutral salt. Calcium naphthenate and the naphthenic acid produced are practically insoluble in water, and exert no decomposing action on cellulose acetate, which is proved by boiling the purified cellulose acetate with water as well as with the naphthenic acid emulsion in water under the same condition, and finding no difference of acetylation degree and copper number between both boiled products. If the cellulose acetate used contains a higher amount of sulphuric acid, the boiled product with the calcium naphthenate emulsion shows a less modification of cellulose and a less decrease in the acetylation degree. The dissociation of naphthenic acid in water nearly negligible, the P_H of 0.05% solution being nearly 6.8. From such observations as above, calcium naphthenate is to be considered as the most reliable stabilizer for cellulose esters.

Calcium naphthenate dissolves in ether and acetone, the viscosity change of the solution with the concentration being shown in Table 4.

TABLE 4

Concentration of calcium naphthenate in ether g/100 cc	Viscosity by flow time in sec measured with Ostwald viscometer		
	(1)	(2)	(3)
0	9.8	9.8	9.2
0.75	10.0	10.0	10.0
1.5	10.0	10.0	10.2
3.0	11.0	10.4	10.6
6.0	12.0	12.2	—
10.0	13.4	14.4	13.2
20.0	19.2	20.0	19.8

The viscosity incresses with the increase in the concentration with a linear function, and therefore the colloidality of calcium naphthenate is not high.

Calcium naphthenate and naphthenic acid are a plastizer of cellulose acetate, though their plastizing action is not remarkable. With the addition of both compounds, amounted to about 1-2 percent on cellulose acetate, the tensile strength and elongation of the cellulose acetate film increases. But when the amount of the addition is greater than 2 percent, the tensile strength and elongation decreases, and when the addition is more than 6 percent, calcium naphthenate or naphthenic acid appears in the film as fine particles.

Calcium naphthenate, as related above, is the most effective stabilizer for cellulose esters, and the optimal amount to be added is supposed to be 1-2 percent on the cellulose esters.

The stabilizing effect ef calcium naphthenate in long years is in the course of experimenting, and though a complete result will be published in a near future, a part of which is shown in Table 5.

TABLE 5

	Properties of cellulose acetate film					
	Elongation, %		Carbonization temp. °C.		Acetic acid evolved, %	
	A	B	A	B	A	B
At preparation	12.3	12.6	182.0	191.0	1.24	0.54
	14.2	15 7	186.5	188.5	2.40	0.41
	13.1	14.3	184.2	200.7	1.84	1.00
After 1 year	8.4	12.4	162.4	192.0	1.86	0.86
	9.6	14.8	171.4	188.5	4.50	1.20
	—	—	156.6	187.2	4.68	0.86
After 1 year and 6 months	5.4	11.4	161.0	188.4	3.64	1.40
	4.4	14.6	154.3	187.2	4.26	1.62
	5.7	—	152.8	185.4	5.00	—

(A) No calcium naphthenate is added.
(B) 2 *g* of calcium naphthenate are added for 100 *g* of cellulose acetate.

The metallic salts of other higher fatty acids or of organic acids of a weak acidity in general may be also used as the stabilizer as calcium naphthenate.

4. Summary

Calcium naphthenate is found to be the most effective stabilizer for cellulose acetate as well as for cellulose nitrate. Calcium naphthenate exerts no adverse action on cellulose acetate, and combines with sulphuric acid, present in cellulose acetate, forming calcium sulphate and naphthenic acid. Naphthenic acid produced exerts also no saponifying action on cellulose acetate, but improves the mechanical properties of the cellulose acetate film. Calcium naphthenate acts also as the plastizer for cellulose acetate. The

amount of calcium naphthenate to be added must be calculated from the amount of the sulphuric acid present in cellulose acetate, but in general cases 1-2 percent on cellulose acetate will be sufficient.

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抄　錄

醋酸纖維素及び其の溶液の研究（第三報）
醋酸纖維素の安定劑

所員　工學博士　田中芳雄
囑託　工學博士　厚木勝基

醋酸纖維素は水洗及中和等により其の含有する酸分を除去し精製し得らるゝけれども、其の精製は相當に面倒であり、又精製の程度も定量的に信賴出來ない。故に痕跡程度の遊離又は遊離され易い酸分が殘るものとして、これを中和又は無害にする安定劑を添加するを安全とする。安定劑としては從來弱アルカリ性化合物例へばアミン類を使用して居るが、醋酸纖維素は弱アルカリにより容易に鹼化さるゝ故に適當の安定劑とは考へられない。

著者等はナフテン酸其他脂肪族の高級有機酸の金屬鹽類が安定劑として最も適當して居る事を發見した。例ばナフテン酸石灰を使用すると硫酸又は醋酸は石灰鹽を作り無害となる。そして他方に出來るナフテン酸は殆と不溶であつて水とエマルジョンにした時の P_H は 6.8 に過ぎない。從て其の酸性は醋酸纖維素に何等の有害作用を及ぼさない。殊にナフテン酸及び其の石灰鹽はドープ中に溶解し且醋酸纖維素に對し可塑劑として作用する。

ナフテン酸石灰の添加量は醋酸纖維素中の酸分の量により異るべきであるが大體醋酸纖維素に對し 1-2% 用ふればよい。

尙ナフテン酸石灰は硝化纖維素に對しても有効なる安定劑である。