Title	Studies on carboxylic-acid type ion exchange resins
Sub Title	
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Publisher	慶應義塾大学藤原記念工学部
Publication year	1952
Jtitle	Proceedings of the Fujihara Memorial Faculty of Engineering Keio University Vol.5, No.19 (1952.) ,p.74(1)- 80(7)
JaLC DOI	
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Notes	
Genre	Departmental Bulletin Paper
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=KO50001004-00050019-0001

Studies on Carboxylic-Acid Type Ion Exchange Resins*

Yasuji OHTSUKA**

Abstract

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acid. The resinous products obtained are separated, washed with
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the degree of swelling.

The some series of cation-exchange resins are prepared by
two-stage process in which sulfuric acid is used as catalyser at
initial condensation and then alkali such as sodium hydroxide and
ammonium hydroxide is added as catalyser for further conden-
sation. Ion exchange resins in this method are lighter-colored
and of high exchange capacity (3. - 4.0 m.eq/g.).

I. Introduction

Carboxylic-acid type ion exchangers which permit extraction and purification
of organic compounds because of their selectivity are of important recently. The
most representiative ones in this series are Wofatit-C[1], Amberlite IRC - 50[2], etc.,
and Oda, Shimizu, and Nakayama[3][4][5] have investigated in this field in Japan.

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1) The Chemical Age 1946, 809
2) R. Knnin, R. E. Barry, Ind. Engi Chem. 41, 1269 (1949)
3) Oda, Shimizu, Nakayama, Chem. High Polymers (Japan) 5, 21 (1948)
4) Oda, Shimizu et al, ibid, 5, 274 (1948)
5) Oda, Shimizu et al, ibid, 6, 14 (1949)

Although it is known that salicylic acid can be condnsed with formaldehyde to produce resinous materials,[6] these are soluble in alkali and not ion exchangeable. In this report salicylic acid-formaldehyde resins as cation-exchangers for extraction of streptomycin are investigated. Phenol is added in order to insolubilize the resins to alkali. Polymerization is catalysed with sulfuric acid, hydrochloric acid, and by two-stage process, that is, with sulfuric acid initially and then alkali.

II. Experiments and Results

I. Sulfuric Acid as a Catalyser

In a three-necked, round-bottomed flask, fitted with a stirrer, a reflux condenser and a thermometer are placed the mixture of salicylic acid (S), phenol (P) and formalin (F). The mixture is warmed in a oil-bath at 80 - 90° C. until the mixture is completely dissolved. To this solntion is added 50 % sulfuric acid with vigorous stirring. The reaction is started, the temperature elevated, and the solution bigins to be cloudy after 5 - 10 minuts. The refluxing is continued for 1 - 4 hrs. to produce resinous material. This is washed with water, pulvilized, and further heated at 100° C. in electric oven or 120 - 130° C. in 15 - 20 mm. Hg. Then, it is immersed in 1N sodium hydroxide over night, filtered, washed with water, until nothing is precipitated when the filtrate is acidified, regenerated by 1N hydrochloric acid, and dried at 100° C. Yield is calculated as follows.

$$\text{Yield}(\%) = \frac{\text{Resin obtained}(g) \times 100}{1.21 \times \text{Phenol}(g) + 1.09 \times \text{Salicylic acid}(g)}$$

After shieving, the particles of 25 - 40 mesh is used on the determination of total exchange capacity in the ordinary manner[7] and swelling. From the results showed on table 1, and Fig. 1 - 6, the conclusions are as follows.
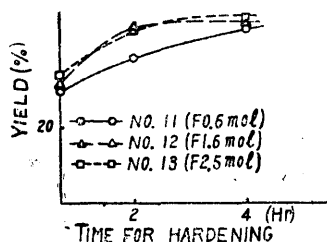

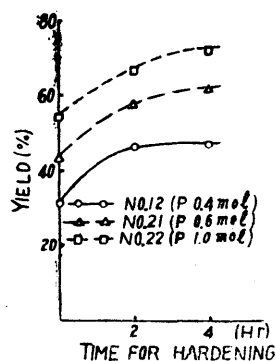Fig. 1. Effect of amownt of F to yield when ratio of S to P is 0.4

Fig. 2. Effect of amownt of P to yield when ratio of F to S is 1.6

6) D. R. P. 339,495

7) R. Kunin, R. E. Barry, Ind. Eng. Chem. 41, 1269 (1949)

Table 1

Exp. No.		Materials (mol.)			Catalyser 50%H_2SO_4 (mol.)	Time of reflux (hr.)	Time for hardening (hr.)	Yield (%)	Cation exchange capacity (m.eq./g.)	Swelling
		Salicylic acid	Phenol	Formal-dehyde						
11	A	1	0.4	0.6	0.5	4	0	30.2	4.16	1.6
	B						0	29.4	4.77	1.6
	C						2	38.4	4.97	1.6
	D						4	45.9	5.12	1.5
12	A	1	0.4	1.6	0.5	4	0	33.7	4.87	1.7
	B						0	31.5	5.16	1.7
	C						2	46.6	4.51	1.7
	D						4	47.1	4.71	1.5
13	A	1	0.4	2.5	0.5	4	0	33.3	3.92	1.5
	B						0	33.9	4.75	1.4
	C						2	45.9	4.56	1.4
	D						4	48.8	4.56	1.4
21	A	1	0.6	1.6	0.5	4	0	43.5	4.56	1.4
	B						0	43.6	4.38	1.4
	C						2	57.8	4.76	1.4
	D						4	61.3	4.20	1.4
22	A	1	1.0	1.6	0.5	4	0	54.1	3.35	1.5
	B						0	54.5	4.03	1.9
	C						2	66.8	4.23	1.4
	D						4	72.1	4.20	1.3
24	A	1	1.0	3.0	0.5	4	0	66.5	3.93	1.5
	B						0	63.3	4.08	1.4
	C						2	73.6	4.06	1.4
	D						4	81.2	3.81	1.4
	E						10	84.9	3.30	1.3
27	A	1	1.0	5.0	0.5	4	0	63.4	3.72	1.4
	B						2	79.4	2.91	1.4
	C						4	82.1	2.36	1.2
	D						6	84.0	2.16	1.2
	E						10	87.9	1.97	1.2
28	A	1	1.0	3.0	0.5	1	0	47.6	3.78	1.5
	B						2	75.0	4.28	1.4
	C						4	82.2	3.62	1.3
	D						6	84.6	3.21	1.2
	E						9	86.6	2.94	1.1
29*	C	1	1.0	3.0	0.5	1	2	77.5	3.69	1.3
	D						4	78.5	3.40	1.2
	E						6	79.5	3.23	1.2
30	C	1	0.6	3.0	0.5	1	2	59.3	4.52	1.4
	D						4	76.8	3.34	1.4
	E						6	77.2	3.34	1.4
31*	C	1	1.0	3.0	0.1	1	2	64.8	3.94	1.4
	D						4	65.6	3.86	1.3
	E						6	65.6	3.92	1.3

* Hardened at 120~130°C, under 15~20mm Hg

(a) Feed ratio

When the ratio of P to S is 0.4, it is showed by Fig. 1 that the yield of resin is poor. When the ratio of F to S is 1.6, the more amount of P, the more is the yield of resin. The ratio of P (crosslinking agent) to S is fixed to unit, and more amount of F is used. Fig. 2 shows that excellent result is obtained when F is 3.0 mol., and that the yield of exchanger does not increase in the experiment using more than 3.0 mol. of F. Moreover, Fig. 4 shows that the result when mol-ratio of P. S and F, is 1 : 1 : 3 is better than 1 : 0.6 : 3. For this reason, if
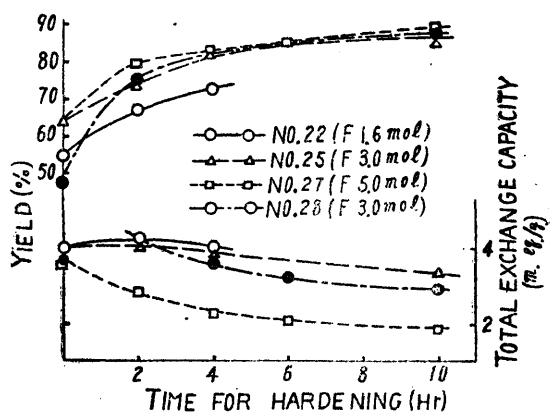
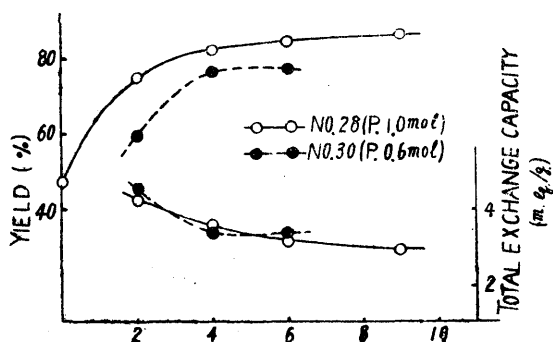Fig. 3. Effect of amount of F to yield when ratio of P to S is 1.0

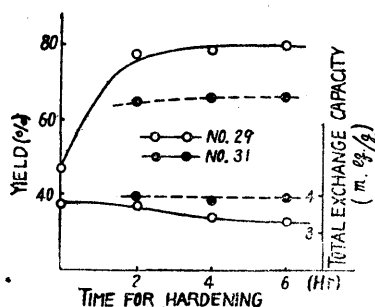Fig. 4 Effect of amount of P to yield when ratio of F to S is 3.0

Fig. 5. Relation between yield and amouut of sulfuric acid
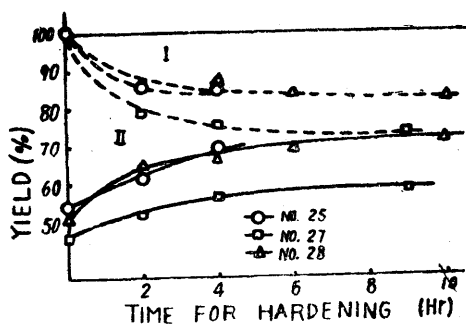

Fig. 6. Effect of hardening process and alkali treatment on yield
I: decreasing amount by hardening
II : alkali soluble part

a quantity of phenol less than equi-mol. of salicylic acid is condensed, the use of feed that mol.-ratio of P. S. and F is 1 : 1 : 3 renders the best result.

(b) Hardening process

As the crude resin obtained after refluxing is soft and partly soluble in alkali, hardening process is necessarily. Fig. 6 shows that the prolongation of duration of hardening decreases alkali soluble part and increases yield of exchanger. Fig. 7 shows that hardening under atmospheric pressure gives more yield than in vacuuo.

(C) Time of refluxing and amount of catalyser

In comparison of Exp. No. 25 (refluxed for 1 hr.) and No. 28 (refluxed for 4 hrs.) in Fig. 3, it is seen that the former g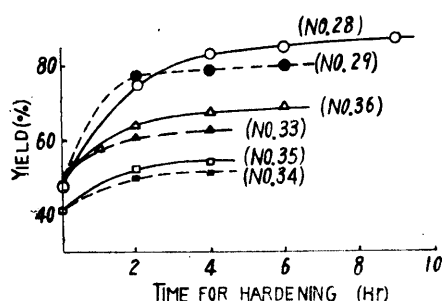ives better yield than the latter during relatively short hardening, but that difference between their yields decreases with prolongation of hardening and disappears in hardening beyond 4 hrs. And so, when the resin further heated longer than 4 hrs., it is sufficient that the reactant is refluxed for 1 hr. Fig. 5 shows that use of 0.5 mol. of sulfuric acid renders more yield of exchanger than 0.1 mol.

Fig. 7. Relation between condition of hardening process and yield

(d) Total exchange capacity and degree of swelling

Total exchange capacity and degree of swelling, volume change in case of exchange, have a tendency to decrease with prolongation of hardening which increases the yield. The maximum of the total capacity is 4.52 m. eq./g. of Exp. No 30 C and the minimum of the swelling is 1.1 of Exp. No. 28F.

II. Hydrochloric Acid as a Catalyser

Using hydrochloric acid as catalyser, the same procedure as sulfuric acid is done. These results are showed in Table 2. Both the yield and the total exchange capacity are worse than the case of sulfuric acid. Moreover, as the yield of extraction of streptomycin has the same tendency, the studies of this case are stopped.

Table 2

Exp. No.		Material (mol.)			Catalyser 12N HCl (mol.)	Time of reflux (hr.)	Time for hardening (hr.)	Yield (%)	Cation exchange capacity (m.eq./g.)
		Salicylic acid	Phenol	Formoldehyde					
42	B	1.0	0.3	1.6	0.8	4	0	17.2	4.05
	C						2	17.2	4.15
43	B	1.0	0.5	1.6	0.8	4	0	27.0	3.78
	C						2	42.1	3.82
44	B	1.0	1.0	1.6	0.8	4	0	29.3	2.51
	C						2	59.9	2.62

III. Case of Two-stage Process

The same series of cation-exchange resins are prepared by two-stage process in which sulfuric acid is used as catalyser at initial condensation and then alkali such as sodium hydroxide and ammonium hydroxide is added as catalyser for further condensation. The mixture of 1 mol. of S, 1 mol. of P, and 3 mol. of F are refluxed in oil-bath for 10-20 min. in the presence of 0.1 mol. of 50% sulfuric acid to produce a white oily or resinous material, then made alkaline with 0.25 mol. of sodium hydroxide or ammonium hydroxide, and further refluxed for 1-4 hrs. .After-treatment is done in the same manner as above described. Table 3 and Fig. 7 show these results. In comparison with the case of sulfuric acid, this process gives poor yield, but the same relations between yield and hardening process and between hardening under atmospheric pressure and in vacuuo are found. Refluxing for 1 hr. gives, in general, better yield than for 4 hrs. The crude resin obtanined in the presence of sulfuric acid after refluxing are light red, but changes dark red during hardening process. In the case of two-stage process, the resin is white innitially, red after alkali treatment, and light yellow after regeneration with hydrochloric acid.

Table 3

Exp. No.		Materials (Mol.)			Catalyser	Fardening reaction			Yield (%)	Cation exchange capacity (m.eq./g.)	Swelling
		Salicylic acid	Phenol	Formal-dehyde							
32	C	1	1	3	H₂SO₄ ∣ NH₄OH	120-130° 15-20 mmHg	2hrs.		54.8	3.52	1.3
	D						4		55.3	3.51	1.3
36	B	1	1	3	H₂SO₄ ∣ NaOH	100-105° normal pressure	0		46.7	3.88	1.5
	C						2		63.7	4.04	1.3
	D						4		67.6	4.00	1.4
	E						6		68.7	3.95	1.3
33	B	1	1	3	H SO₄ ∣ NaOH	120-130° 15-20 mmHg	1		58.1	3.90	1.4
	C						2		60.9	3.96	1.3
	D						4		62.2	4.02	1.3
34	C	1	1	3	H₂SO₄ ∣ NaOH	120-130° 15-20 mmHg	2		50.0	3.92	1.3
	D						4		51.5	3.83	1.3
35	B	1	1	3	H₂SO₄ ∣ NaOH	100-105°C normal pressure	0		41.0	4.00	1.3
	C						2		52.4	3.89	1.3
	D						4		54.2	3.93	1.3

Reflux time : Nos. 32, 34, 35 — 1 hr.
Nos. 33, 36, — 4 hrs.

Summary

As cation exchanger for streptomycin-extraction, salicylic acid-formaldehyde

resins are prepared under various conditions. Phenol is added as cross-linking agent.

Polymerization is catalysed, (1) with sulfuric acid, (2) with hydrochloric acid, and (3) by two-stages process, that is, with sulfuric acid initially and then with alkali. On these three cases, experiments are made under various conditions relating to the proportion of P (phenol) : S (salicylic acid) : F (formaldehyde), the amount of catalyser and the time of reaction. Exchange capacity, volume-change in case of exchange and yield are determind. Among above three, sulfuric acid gives the best yields and the highest exchange capacity.

In case of sulfuric acid as catalyst, following results are obtained.

(1) The proportion of P : S : F = 1 : 1 : 3 (when fixed at P : S = 1 : 1) gives the optimum result.

(2) As the time of reaction, one hour is sufficient.

(3) 0.5 mol. of sulfuric acid (50%) gives better results than 0.1 mol.

(4) The maximum exchange capacity is 4.52 m.eq./g.

Experiments on the extraction of streptomycin using the above resins will be described in the next report.

Acknowledgment