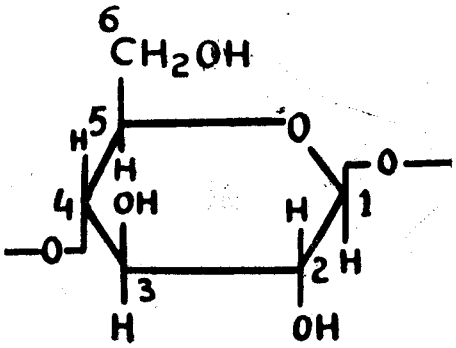
Cellulose Derivatives Part I Na-C.M.C. From Waste Paper

G. SHAKER
JAGRAJ SINGH CHAWLA

Cellulose can be chemically modified to give products of specialised properties of industrial importance. Cellulose molecule contains three reactive hydroxyl groups in each anhydro D-glucopyranose unit. It is, therefore, theoretically possible to substitute three hydroxyl groups at position 2, 3 and 6 with other substituent and the product would thus be described as having degree of substitution (D. S.) 3.0.



These active hydroxyl can be etherified by organic halides, alkene oxides, or olefine activated by polar substituent groups in the presence of alkali. The most important cellulose ether is the carboxymethyl cellulose (C. M. C.) or rather its water soluble sodium salt.

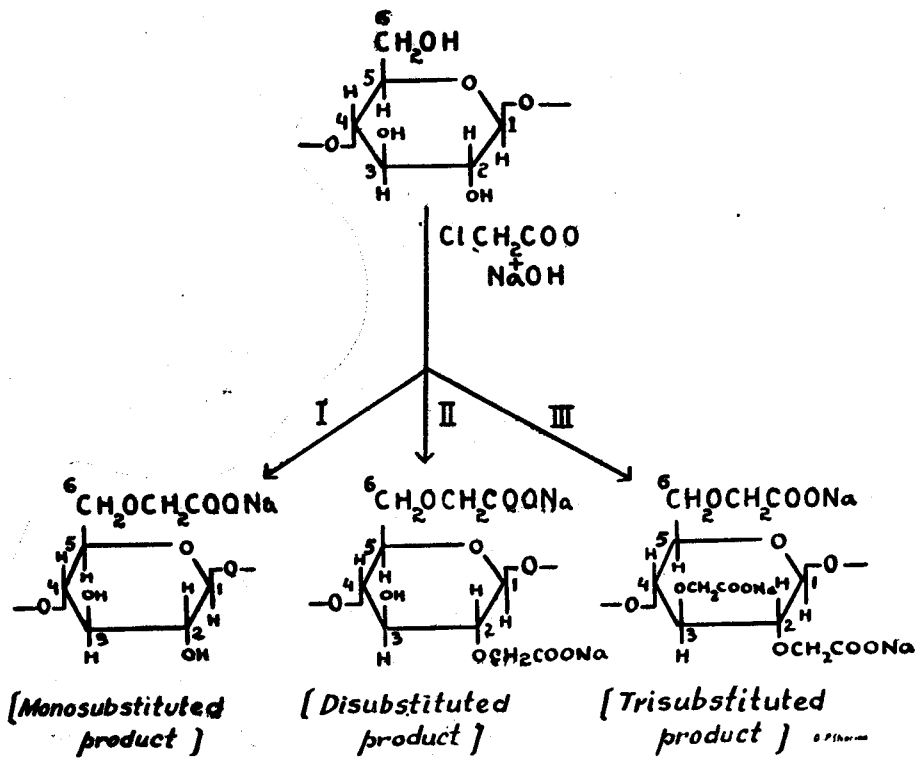
Water soluble C. M. C. is obtained by treating the alkali cellulose with mono-chloroacetic acid in dispersing medium like tertiary butyl alcohol, isopropyl alcohol, ethyl alcohol or methyl alcohol.

G. Shanker and Jagraj Singh Chawla
Regional Research Laboratory,
Jammu-Tawi

Commercial sodium C. M. C., generally has an average degree of substitution of less than 1.3, but for convenient handling of the flow properties the D. S. is kept between 0.4-0.8. D. S. of less than 0.3 is water insouble but soluble in 6% alkali solution. Na-C.M.C. is water soluble thixotropic substance which finds application as an industrial gum in pharmaceuticals, ceramics, foundry, textile, paper pulp and drilling etc.

Variation of Solublity of Cellulose Ethers with Degree of Substitution

Solubility	Methyl cellulose	Ethyl cellulose	Na-C.M.C.
4—8% NaOH	0.1-0.6	0.5-0.7	0.05-0.25
Cold Water	1.3-2.6	0.7-1.3	0.3-0.8
Increasing in alcohol	2.1-2.6	1.4-1.8	2.0-2.8
Increasing in solvents	2.4-2.7	1.8-2.2	—
Increasing in hydrocarbons	2.6-2.8	2.7-2.9	—



Flow Properties of Sodium Carboxymethyl Cellulose

Viscosity type	D. S.	Solution conc. %	Brookfield range Cps.
Low	0.7-0.8	2.00	1-100
Medium	0.7-0.8	2.00	10-1000
High	1.2	2.00	40-4000
High	0.7-0.8	1.00	1000-1,00,000

Raw materials

The main raw material used for the manufacture is purified wood pulp or purified cotton linters. The present investigation is undertaken to utilise the waste paper for the preparation of Na-C. M. C. Utilisation of wast paper is not new and U.S.A. and Japan, are the world's largest users of waste paper for paper making. Attention has also been given to find the possibility of utilisation of waste paper in other than conventional paper making for power generation, for conversion of cellulose to yeast and edible protein for animal food, for the production of sugars, alcohols, oils as well as for the manufacture of panel, insulating boards and other substitutes for wood based articles.

Waste papers viz. book paper, stationery cuttings are available at a cost much lower than any other source of cellulose. This paper reports the preparation of Na-C.M.C. from waste paper.

Experimental procedures

1. The starting materials used for the present studies were (I) Waste book paper (unbleached and bleached) (II) Stationery cuttings and (III) Whatmann filter paper (as reference material for comparative study).

I. (a) **Waste book paper —**

These were shredded and then treated with 2% sodium hydroxide solution (material liquor ratio 1:10) and kept overnight Thereafter it was thoroughly washed with water over 40-60 mesh sieve till free from alkali, dried and yield noted. This formed the starting material for the preparation of Na-C.M.C,

(b) **Pretreatment of waste—**

This was same as I (a) except that after the above treatments, a bleaching treatment was carried out with 1% sodium hypochlorite solution at pH of 8.5 for one hour. The sample after-wards was washed free of hypochlorite and alkali by washing with distilled water before drying and noting the yield. This formed another starting material for the preparation of sodium carboxy-methyl cellulose.

II. **Stationery Cuttings :**

These were simply boiled for three hours in excess of water, then dried, weighed and used for the preparation of Na-C.M.C

III. **Whatmann paper :** This was shredded and then used as much for the preparation of sodium carboxymethyl cellulose.

2. **40% Sodium hydroxide treatment of the above samples :** In order to study systematically the effect of alkali on the fillers present in waste matrials, all the above samples were given a treatment with a solution of 40% sodium hydroxide for 45 minutes. After which they, were washed free of alkali, dried at 105°C and yield noted down before analysis.

3. **Removal of hemicelluloses and fillers :** With a view to economise the use of mouochloroacetic acid for the preparation of Na-C.M.C. the book paper waste (unbleached) and waste from the stationery cuttings were given a pretreatment with 18% sodium hydroxide solution at room temperature for 15 minutes to remove the undesirable polysaccharides like hemicelluloses, other short chain cellulose molecules and fillers etc.

4. **Treatment with 18% Sodium hydroxide for various periods :** The treatment with 18% sodium hydroxide solution was given to waste book paper and stationery cuttings (material liquor ratio=1:25). Samples were analysed after 5, 10, 25 and 30 minutes treatment and studied for yield and alpha content.

5. **Degree of substitution of Na-C.M.C. at various timings :** In order to study the effect of reaction time at 55°C on the degree of substitution, samples of Na-C.M.C. were taken out at intervals of 3.5, 5.0 and 7.0 hours of reaction with monochloroacetic acid, add the D.S. determined.

6. **Preparation of sodium curboxymethyl cellulose :** The method followed is essentially that of Swenson with the slight modification that instead of isopropyl-alcohol, ethyl alcohol was used as suspending medium for the preparation of Na-C.M.C. 100 g of the cellulose was taken in 1500 ml of

95% ethyl alcohol and treated with 430 ml of 40 % solution of sodium hydroxide. The alkali solution was added slowly with constant stirring in a period of 1 hour. Then 150 g of mono chloroacetic was added and the stirring continued for another half an hour. This was then kept at 55°C for 4 hours. The product afterwards was filtered over a buchner funnel and washed with 70% ethyl alcohol 5-6 times and the yield of the product was determined after drying.

7. Detailed analysis of various samples

(a) **Moisture content**–The moisture content of all the various samples was studied by keeping the respective samples at 105°C till constant weight.

(b) **Solubility in water** ; Solubility in water was found by dissolving 2.0 gms of the sample of Na-C.M.C. in 100 ml of distilled water at room temperature.

(c) **Gum powder** : The gum powder of various Na-C.M.C. samples was determined by study of the adhesion of these gums to surfaces like glass, wood, wall and paper. This was done by making a paste of the derivative and applying it to the paper slip. This slip was then pasted on various above surfaces and allowed to get dry. For all the cases, it was noticed that the slip remained stuck firmly. This way the gums were found to have excellent gum power.

(d) **Refractive Index** : Refractive Index of the 2 % aqueous Na-C.M.C. solutions was determined by using Abbe's refractometer.

(e) **Specific Gravity** : Specific gravity of the 2% aqueous solution of vraious Na-C. M. C. samples was determined by using a specific gravity bottle.

(f) **Active content** : Active content of the derivative was determined by Rodney's method. About 3-4 gm of Na-C.M.C. was dissolved in hot 80% ethyl alcohol. After about 10-15 minutes, it was filtered in G_2 sintered funnel and the residue was washed with 80% ethyl alcohol 3 times followed by two washings with 95% ethyl alcohol. It was then dried to constant weight at 105°C. The percentage weight of the residue indicated the percentage of the active content present in Na-C.M. C. sample.

(g) **Degree of substitution** : To determine the degree of substitution a known weight 1-2 gm of the active content of the Na-C.M.C. obtained as above (f) was incinerated in a furnace and the ash thus obtained was dissolved in double distilled water and then titrated against 0.1 N sulphuric acid using methyl red as an indicator. Near the end point, the solution was boiled to dispel carbon dioxide and the titration continued, till a distinct end point was obtained.

(h) **Amount of sodium chloride in the Ash of active content**

To determine the residue sodium chloride present in the ash of the active content of Na-C. M. C., a known volume of the above mentioned ash solution (g) was titrated against standard silver nitrate solution using potassium chromate as indicator. The weight of sodium chloride thus determined was subtracted from the weight of the active content taken for analysis and degree of substitution was found as follows;—

$$\text{Degree of substitution} = \frac{0.162\ B}{1-0.8B}$$

Where B=0.1 x b/c

and b=no. of ml of 0.1 N sulphuric acid used

C=weight in grams of residue taken.

(i) **Amount of sodium chloride in Na-C.M.C.** : This was determined by taking 5.0 g of the oven dry sample into a 250 ml beaker. 50 ml of water and 5 ml of hydrogen peroxide (30%) was added and heated for about 15-20 minutes with stirring to dissolve the whole substance. It was then cooled, 100 ml of water added and titrated against 0.1 N silver nitrate till the colour of the precipitate just changed to red. Sodium chloride content was estimated as follows ;

TABLE 1

Analysis of waste Materials.

S.No.		1 (a)	1 (b)	2	3
1.	Moisture %	7.70	6.80	16.00	6.00
2.	Ash %	16.35	7.77	9.45	—
3.	Alcohol–Benzene Extract% (1:2 by vol.)	3.10	2.50	3.20	0.30
4.	Alphacellulose %	63.10	74.80	66.95	95.40
5.	Pentosans %	16.20	13.30	21.90	3.06

1. (a) Book Paper (unbleached); 1. (b) Book paper (bleached)
2. Stationery Cuttings; 3. Whatmann filter paper.

TABLE 2

Characteristics of Sodium Carboxymethyl cellulose obtained from different sources

S.No.		1 (a)	1 (b)	2	3	Commercial
1.	Moisture %	25.17	19.83	13.80	18.03	9.60
2.	Ash %	22.00	18.18	17.40	13.11	41.10
3.	Yield %	145.00	140.00	140.00	150.00	—
4.	pH (2% aq. Sol.)	9.50	10.00	7.50-8.00	6.50-7.00	7.00-7.50
5.	Refractive Index (2% aq. sol.)	1.334	1.335	1.334	1.334	1.335
6.	Specific Gravity (2% aq. sol.)	1.0405	1.0406	1.041	1.055	1.042
7.	Active Content %	65.00	68.20	66.20	79.00	59.00
8.	Degree of substitution (D. S.)	0.66	0.69	0.62	0.75	0.76
9.	NaCl Amount (in Na-C.M.C. sample) %	16.10	14.10	11.20	9.45	21.80
10.	NaCl Amount (in ash of active Content) %	6.80	5.70	3.40	3.42	7.70
11.	Viscosity (Cps) (2% aq. sol.)	43.40	38.00	42.00	65.10*	58.60
12.	Intrinsic Viscosity (dl/g)	3.40	3.30	3.60	4.50	—
13.	Degree of polymerization (D. P.)	340.00	330.00	360.00	450.00	—
14.	Colour	Medium Grey	Pale Grey	Light Cream.	White	Light Cream.
15.	Gum power	Very good	Very good	Very good	Very good	Very good.
16.	Solubility	fairly good	good	Good	Very good	Very good.

1 (a) Book Paper (unbleached) ; 1 (b) Book paper (bleached) ; 2 Stationery Cuttings
3 Whatmann filter paper ; *1 % aq. Sol.

Sodium Chloride %

$$= \frac{A \times N \times 584.5}{G \times (100\text{-}B)}$$

Where A = ml. of Ag No_3 solution added (0.1N)

N = Normality of Ag No_3 solution

G = gms of sample used,

B = % moisture, determined on a separate sample

and 584.5 = gm. molecular weight of NaCl x 10

(j) **Viscosity** : It was determined by preparing 2% aqueous solution of various Na-C.M.C. samples in distilled water and then measuring the time of flow through a capillary type Oswald's Viscometer at a temperature of 25°C and viscosity expressed as sentipoises.

(k) **Intrinsic viscosity** : For the

TABLE 3

Sodium Carboxymethyl cellulose from Waste after 18% Sodium Hydroxide solution treatment-for 15 Minites

S.No.		1	2
1.	Moisture %	12.00	11.40
2.	Ash %	15.20	14.10
3.	Yield* %	111.00	116.00
4.	pH (2 % aq. Sol.)	7.50-8.00	8.20
5.	Refractive Index (2 % aq. sol.)	1.333	1.334
6.	Specific Gravity (2 % aq. sol.)	1.040	1.041
7.	Active Content %	63.00	66.00
8.	Degree of Substitution (D. S.)	0.60	0.62
9.	NaCl Amount (in NaC.M.C. sample) %	12.10	10.30
10.	NaCl Amount (in ash of active Content) %	3.80	3.45
11.	Viscosity (2% aq. Sol.) Cps.	35.00	40.00
12.	Intrinsic viscosity (dl/g)	3.15	3.20
13.	Degree of Polymerization (D. P.)	315.00	320.00
14.	Colour	Light Grey	Light cream.
15.	Gum power	good	good
16.	Solubility	Good	Good

1 Book Paper ; 2 Stationery Cutting ; * Based on original oven dry wt. of Waste.

determination of intrinsic viscosity of any particular Na-C.M.C. aqueous solutions of the sample at various concentrations was prepared. The time of flow through the capillary type Oswald's viscometer of these solutions was noted down. From the data obtained, the intrinsic viscosity (expressed in deciliter/gm) was found by the standard extrapolation procedure.

(l) **Other constituents** : Other chemical constituents viz. pentosans, alphacellulose, ash and alcohol benzene solubles of the materials were estimated according to Tappi methods.

Results and Discussion

Results of chemical examination of the untreated raw materials are given in Table 1. As can be seen the ash content and alcohol benzene extractives varied between 9.5 to 16.35 and 3.10 to 3.20 respectively. These are mainly due to the fillers and the sizing materials present in the raw material.

Comparative study of the Na-C. M. C. samples obtained from different cellulose sources and the commercial Na-C.M.C. is given in Table 2. Active content is 79% in Na-C.M.C. prepared from Whatmann paper. Viscosity of Na-C.M.C. from waste paper ranged between 38.0 to 43.4 with degree of substitution 0.62 to 0.69 which fall under medium range. Treatment of waste paper with 18% sodium hydroxide solution for 15 minutes prior to the reaction with the monochloroacetic acid resulted in the lowering of the ash content due to the removal of fillers. The lower yield of the Na-C.M.C. based on the original waste paper was probably due to the removal of hemi-

TABLE 4.

Analysis of Waste after 40% Sodium Hydroxide Solution Treatment for 45 minutes.

S.No.		1 (a)	1 (b)	2	3
1.	Yield %	85.00	80.00	85.00	120.00
2.	Ash %	3.33	2.95	5.00	2.07
3.	Alcohol-Benzene (1:2 by Vol.) Extract %	1.40	1.32	1.20	0.20
4.	Alphacellulose %	89.60	91.00	89.30	97.00
5.	Pentosans %	5.03	4.75	4.12	1.22

1 (a) Book Paper (unbleached) ; 1 (b) Book Paper (bleached)
2 Stationery Cuttings ; 3 Whatmann filter paper.

TABLE 5

Yield and Alphacellulose Content at different treatment timings with 18 % sodium hydroxide solution

Time (min.)	Yield and Alpha cellulose Content %		Calculated alphacellulose Content %	
	1	2	1	2
5	83.00	94.50	75.00	70.00
10	81.30	86.20	78.00	77.90
25	68.00	69.10	93.00	97.00
30	63.10	66.85	100.00	100.00

1 Book Paper (unbleached) ; 2 Stationery cuttings.

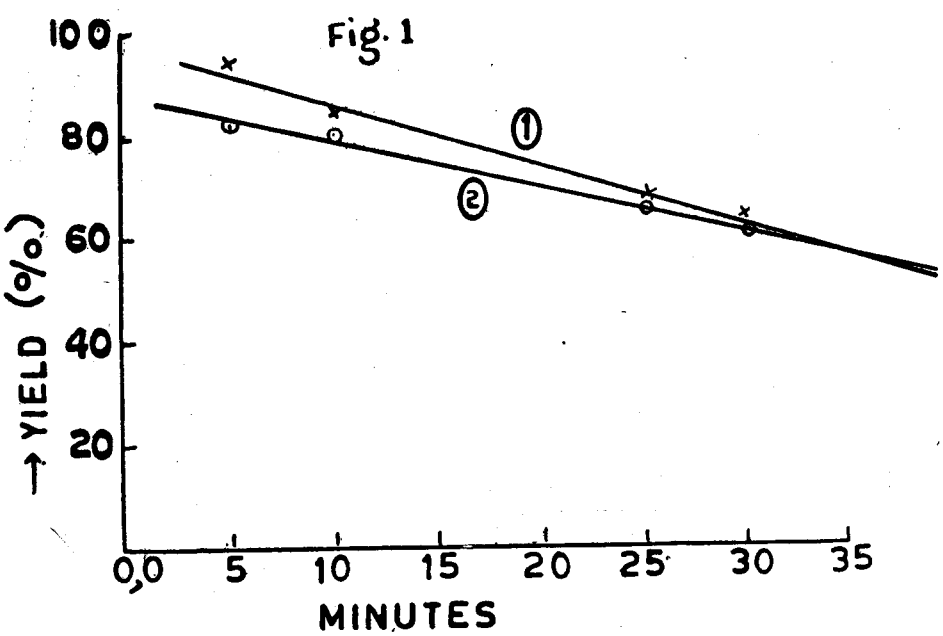


Fig. 1—Relationship between yield of the sample after treatment with 18% sodium hydroxide solution with time.
(1) — × — × — Stationery Cuttings.
(2) — ⊙ — ⊙ — Book paper (unbleached)

celluloses and other short chain cellulose molecules (Table 3). Gradual Addition of 40% sodium hydroxide solution for the process of reaction with chloroacetic acid was found to reduce considerably fillers and other polysaccharides in a period of 45 minutes and this eliminated the unnecessary materials in the final product (Table 4). Additional bleaching treatment with 1% sodium hypochlorite for 1 hour also helped to reduce both ash, extractives and pentosan content.

The effect of the sodium hydroxide solution (18%) at various periods on the yield and alpha content are given in Table 5 and Figures 1-3. The effect of different reaction timings at constant temperature on the degree of substitution is given in Table 6 and Figure 4.

Since the waste paper does not possess high alpha cellulose, the treatment of the material prior to monochloroacetic acid reaction with 18% alkali solution produced high alpha and thus saved the extra quantity of monochloroacetic acid needed for its preparation, which

TABLE 6

Degree of Substitution at Various Times of Heating at 55°C

Time (hrs.))	Degree of Substitution of NaC.M.C. 1	2
3.5	0.66	0.62
5.0	0.68	0.66
7.0	0.71	0.69

1 Book Paper (unbleached)
2 Stationery cuttings.

otherwies may react with other polysaccharide like hemicelluloses

Fig. 2

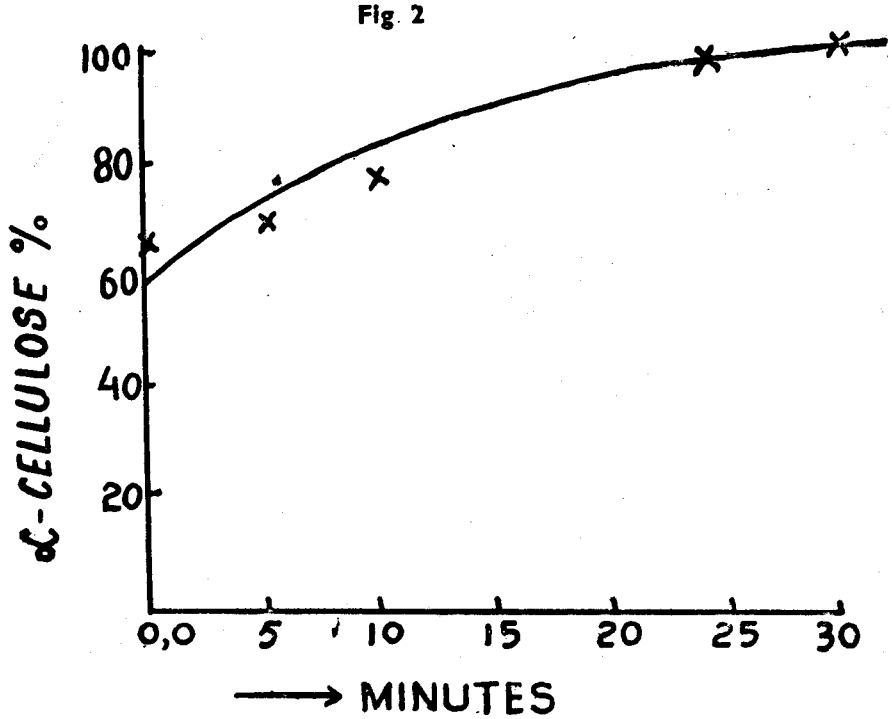


Fig. 2—Relationship betweeen calculated—alphacellulose (%) versus time of 18 % sodium hydroxide solution treatment of stationery cuttings.

Fig. 3

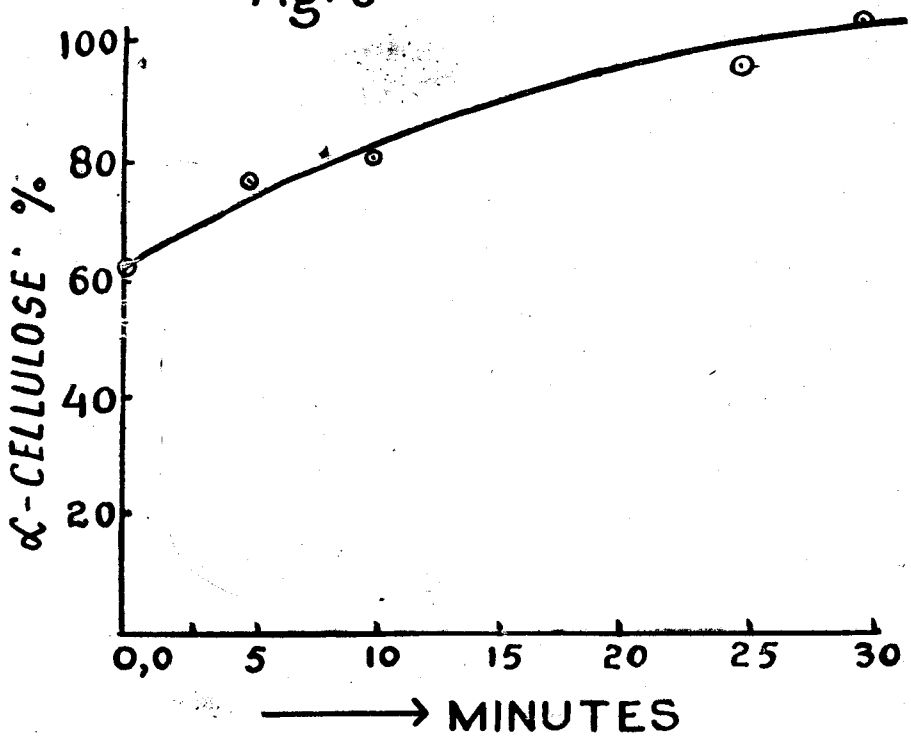


Fig. 3—Relationship between calculated alphacellulose (%) versus time of 18 % sodium hydroxide solution treatment of book paper (unbleached).

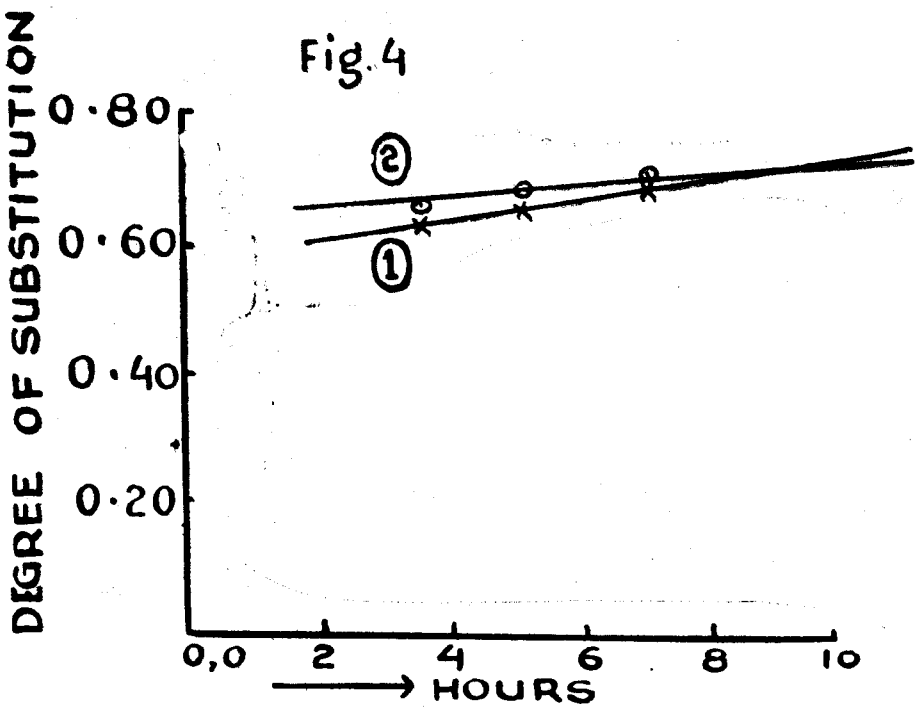


Fig. 4—Relationship between degree of substitution and reaction time.
(1) — × — × Stationery cuttings.
(2) — ⊙ — ⊙ —Book paper (unbleached)

and short chained cellulose molecules.

The light grey colour of the Na-C. M.C. from book paper was mainly due to the presence of some ink particles which remained even after the alkali and bleaching treatments. The colour of Na-C.M.C. from stationery cuttings was light yellow.

Conclusion

The Na-C.M.C. from these cheap waste sources can be prepared safely which can be used as a substitute for cheap gums and in ceramic, oil drilling, foundry and other industries where colour and purity are not the main considerations. Taking into account the losses effected after the removal of fillers and noncellulosic polysaccharide etc., which get solubilised in alkali solution during the process of reaction, the remaining cellulsose left over constituting to the extent of 60–70%, still forms the cheapest source for the preparation of Na-C.M.C. compared to the other sources based on the original cost of untreated material. The question of availability of bulk supplies of waste paper requires thorough survey and investigation. But it is feasible to have a small scale unit for the utilization of these waste materials.

References

1. Whistler, R. L. : "Industrial Gums" New York : Academic Press, 1959, P 643.
2. Ott, E. and Spurlin, H. M. : "Cellulose and cellulose derivatives" New York : Interscience, 1954, Vol. II & III, P 937-45 & 1465-68.
3. Atchison, J. E. : et al., Paper Trade Journal, **155**,58-64 (1971).
4. Macleod, M. : Paper Trade Journal, **155**, 84 (1971).
5. A. S. T. M. : Standards, Part 15, 496–506 (1966).
6. Swenson, H. A. : unpublished laboratory notes, The Institute of paper chemistry, 1963, in "Methods of Wood chemistry" (B. L. Browning, Ed) New York. Interscience, 1967, Vol. II, P. 490.
7. Dhariyal, C. D. : and Chipalkatte, V. B. in "Cellulose Research" Symposium II (C.S.I.R., New Delhi), 1958, P 121.
8. Rodney, N.H.: et al., Ind. Eng. Chem., **44**, 2811 (1952).
9. Whistler, R. L. : "Methods in Carbohydrate Chemistry" New York : Academic Press, 1963, Vol. III, P 210.
10. Tappi standards and suggested methods.