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Optimisation of conditions of synthesis of oxidised starch from corn and amaranth for use in film-forming applications

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Gum arabic is used as an encapsulating agent because of its film-forming ability. However, India has to import gum arabic for its domestic requirement. Oxidised starch has been reported as a substitute for gum arabic but no data are reported on the exact conditions of oxidation of starch or the analytical indicators for determining the suitability of the product for such a purpose. This work reports on the effect of process conditions for oxidation of corn and waxy amaranth starch with film-forming ability as the major criterion. The process was followed using the analytical indicators of oxidation such as carboxyl content, chlorine consumption and ferricyanide number. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

The oxidised starches of commerce consist of granules whose molecules have been attacked in a heterogenous topochemical fashion. The method of oxidation and recovery of product is different for different oxidants. Raw materials for oxidised starch have varied from dent corn to grain sorghum, waxy maize, sago, potato, rice, wheat, cassava and tapioca (Whistler & Pyler, 1968; Van den Aarsen & Beenackers, 1980; Boruch, 1985; Hebeish *et al.*, 1992). Hydrogen peroxide (Harmon *et al.*, 1971; Kuznetsova & Tregubov, 1984; Kuznetsova *et al.*, 1985; Floor *et al.*, 1989), periodic acid (Kerr, 1950) and sodium hypochlorite have been the most widely used oxidants, each having its advantages and disadvantages.

For hypochlorite oxidised starch the variables are temperature, pH, hypochlorite and starch concentration, inorganic salts and reaction by-products (Schmorak *et al.*, 1962; Potze & Hiemstra, 1963).

Oxidised starch finds a number of applications in the food industry where a neutral tasting, low viscosity 'body builder' is required in lemon curd manufacture, salad creams, mayonnaises, etc. Oxidised starch mixed with about 5% sodium alginate has been reported to replace about 80% of the agaroid used in the formulation of jelly marmalades with no loss of quality (Zubrev *et al.*, 1973). Its other applications in foods include as a bread improver (Shkvarkina & Konenkova, 1975), as a coating for food products to prevent drying out of food and improve appearance (Smid *et al.*, 1971), as an agar substitute in the production of fruit paste candies (Bondareva *et al.*, 1983), as a food thickener (Miyake *et al.*, 1978), as an anti-fouling agent in heat exchangers (Yotsuya *et al.*, 1985) and in the preparation of rice cookies (Takahashi *et al.*, 1970). All of these processes have been patented. Oxidised starch has been developed as a substitute for gum arabic (Miyazaki & Endo, 1986), as a possible wall material for spray dried flavours (Bangs & Reineccius, 1988 Eden *et al.*, 1989) and for use in gum drops (Voelker & Thieme, 1972) but no reported data are available on the exact conditions used for the oxidation of starch or the analytical indicators for determining the suitability of the product for such a purpose.

The present work attempts to study the optimisation of the process for the preparation of oxidised starch from waxy *Amaranthus paniculatas* (Rajgeera) and non-waxy corn starch, with a view to exploring oxidised starch as a film-forming agent and thereby as a gum arabic substitute. The oxidised starches thus prepared have been analysed for the degree of oxidation in terms of carboxyl content, ferricyanide number and chlorine consumption. Their yield and film-forming ability have been tested.

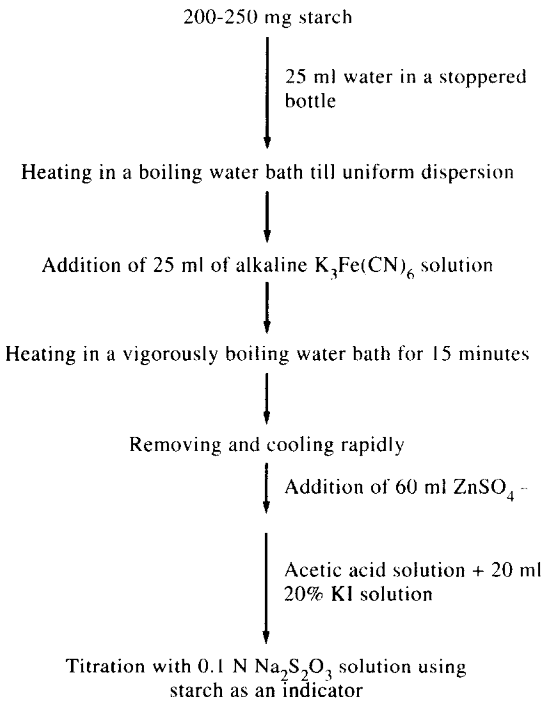
MATERIALS AND METHODS

Corn starch was obtained from M/S Laxmi Starch Pvt. Ltd, Bombay. Starch from locally purchased *Amaranthus paniculatas* was isolated by the alkali steeping method (Yanez & Walker, 1986). Sodium hypochlorite containing 4–6% active chlorine was purchased from M/S Polypharma Ltd, Bombay. The experimental methodology was as follows.

Optimisation of the process for the production of oxidised starch

A four-necked glass reactor assembly was used for studying the process. A starch–water suspension was treated by dropwise addition of sodium hypochlorite solution at a fixed pH for a fixed time and temperature inside the reactor. After the fixed reaction time, starch was separated by vacuum filtration or centrifugation, washed till free of chlorine (tested by using 0.1 N silver nitrate solution) and dried in an oven at 50–55°C.

The effect of process parameters such as pH, concentration of the oxidant (NaOCl) per gram of the starch, time, temperature, mode of addition of hypochlorite, starch:water ratio, effect of catalyst ($MgCl_2$) and final pH of the starch oxidation was studied. The percentage yield of the product on the basis of the raw starch used and the film-forming property were the criteria for studying the process for corn and amaranth starch. The conditions used for both these starches in different trials are shown in Tables 1 and 2. The parameter range given in Tables 1 and 2 was selected on the basis of some trial experiments shown in these tables.



Flow sheet for the determination of reducing value.

Determination of degree of oxidation

This was followed in terms of the following:

Reducing value as ferricyanide number (Schoch, 1964)
The method used is shown below. Simultaneously a blank titration was performed without starch and the ferricyanide number was calculated as follows:

$$\text{Ferricyanide no.} = \frac{(\text{Blank} - \text{Sample})\text{ml} \times \text{Normality of thio} \times 10}{\text{Sample weight (dry basis) in g}}$$

Carboxyl content
This was determined as per the procedure of Mattisson & Legendre (1952). To 0.5–1.0 g of starch, 25 ml 0.1 N HCl was added and the mixture was allowed to stand for 30 min with occasional stirring. The slurry was filtered through a fritted glass crucible (G 4) and washed with distilled water until it was free from chlorine. The starch was then transferred to a 500 ml beaker to which 300 ml distilled water was added. It was then boiled for 5–10 min for complete gelatinisation, followed by titration with 0.1 N NaOH solution with phenolphthalein as indicator. A blank test was also performed with unmodified starch. Carboxyl content was calculated as follows:

$$\text{milli-equivalents of acidity/100g stench} = \frac{(\text{Sample} - \text{Blank})\text{ml} \times \text{Normality of NaOH} \times 100}{\text{Sample weight (dry basis) in g}}$$

Apparent % carboxyl = milliequivalents of acidity/ 100 g starch × 0.045.

Determination of chlorine consumption

Chlorine consumption, expressed as grams of Cl_2 per gram of starch (g Cl_2/g starch) was determined following the procedure of Hebeish *et al.* (1989). In this method, the decrease in hypochlorite concentration due to oxidation of starch was determined from the difference between the concentration of 'blank' solution without starch and solution containing starch at the end of the reaction. Hypochlorite concentration was determined by titrating 10 ml of the solution with 0.1 N $Na_2S_2O_3$ solution after addition of 10 ml 10% solution and 5 ml glacial acetic acid. The amount of chlorine consumed was calculated as follows:

$$\text{g } Cl_2/\text{gstarch} = \frac{(\text{Blank} - \text{Sample})\text{ml} \times V \times N \times 35.5}{10 \times W \times 1000}$$

where V is the volume of NaOCl used for oxidation, N is the normality of the $Na_2S_2O_3$ solution and W is the weight of dry starch.

Table 1. Conditions selected for optimisation of oxidised starch from corn starch

Trial no.	Starch (g)	Water (ml)	pH±0.1	NaOCl concentration (g/g of starch)	Mode of addition of NaOCl	Time (min)	Temperature (°C)	Final pH
1	25	75	7.0	0.15	Over 90 min	120	30	7.0
2	25	75	7.5	0.15	Over 90 min	120	30	7.0
3	25	75	8.5	0.15	Over 90 min	120	30	7.0
4	25	75	8.5	0.15	Over 90 min	120	30	7.0
5	25	75	9.0	0.15	Over 90 min	120	30	7.0
6	25	75	7.5	0.05	Over 90 min	120	30	7.0
7	25	75	7.5	0.10	Over 90 min	120	30	7.0
8	25	75	7.5	0.15	Over 90 min	120	30	7.0
9	25	75	7.5	0.20	Over 90 min	120	30	7.0
10	25	75	7.5	0.25	Over 90 min	120	30	7.0
11	25	75	7.5	0.15	Over 60 min	90	30	7.0
12	25	75	7.5	0.15	Over 90 min	120	30	7.0
13	25	75	7.5	0.15	Over 120 min	150	30	7.0
14	25	75	7.5	0.15	Over 45 min	60	30	7.0
15	25	75	7.5	0.15	Over 60 min	90	30	7.0
16	25	75	7.5	0.15	Over 90 min	120	30	7.0
17	25	75	7.5	0.15	Over 120 min	120	30	7.0
18	25	62.5 (1:2.5)	7.5	0.15	Over 90 min	120	30	7.0
19	25	75.0 (1:3)	7.5	0.15	Over 90 min	120	30	7.0
20	25	87.5 (1:3.5)	7.5	0.15	Over 90 min	120	30	7.0
21	25	*100 (1:4)*	7.5	0.15	Over 90 min	120	30	7.0
22	25	75	7.5	0.15	All at a time	120	30	7.0
23	25	75	7.5	0.15	Over 30 min	120	30	7.0
24	25	75	7.5	0.15	Over 60 min	120	30	7.0
25	25	75	7.5	0.15	Over 90 min	120	30	7.0
26	25	75	7.5	0.15	Over 120 min	120	30	7.0
27	25	75	7.5	0.15	Over 90 min	120	25	7.0
28	25	75	7.5	0.15	Over 90 min	120	30	7.0
29	25	75	7.5	0.15	Over 90 min	120	35	7.0
30	25	75	7.5	0.15	Over 90 min	120	35	7.0
31	25	75	7.5	0.15	Over 90 min	120	35	6.5

Table 2. Conditions selected for optimisation of oxidised starch from amaranth starch

Trial no.	Starch (g)	Water (ml)	pH±0.1	NaOCl concentration (g/g of starch)	Mode of addition of NaOCl	Time (min)	Temperature (°C)	Final pH	Catalyst used ($MgCl_2$ 0.0115 g/g of starch)[a]
1	15	45	7.0	0.025	Over 45 min	60	30	7.0	—
2	15	45	7.0	0.05	Over 45 min	60	30	7.0	—
3	15	45	7.0	0.10	Over 45 min	60	30	7.0	—
4	15	45	7.0	0.15	Over 45 min	60	30	7.0	—
5	15	45	7.0	0.20	Over 45 min	60	30	7.0	—
6	15	45	7.0	0.25	Over 45 min	60	30	7.0	—
7	15	45	7.0	0.10	Over 45 min	60	30	7.0	—
8	15	45	7.0	0.10	Over 60 min	90	30	7.0	—
9	15	45	7.0	0.10	Over 90 min	120	30	7.0	—
10	25	75	7.5	0.25	Over 90 min	120	30	7.0	—
11	15	45	7.0	0.10	Over 120 min	150	30	7.0	—
12	15	45	7.5	0.10	Over 120 min	150	30	7.0	—
13	15	45	8.0	0.10	Over 120 min	150	30	7.0	—
14	15	45	8.5	0.10	Over 120 min	150	30	7.0	—
15	15	45	9.0	0.10	Over 120 min	150	30	7.0	—
16	15	45	9.0	0.10	Over 120 min	150	30	7.0	—
17	15	45	9.0	0.10	Over 120 min	150	30	7.0	+
18	15	45	9.0	0.10	Over 90 min	120	30	7.0	+
19	15	45	9.0	0.10	Over 60 min	90	30	7.0	+
20	15	45	9.0	0.10	Over 45 min	60	30	7.0	+
21	15	45	8.0	0.10	All at a time	120	30	7.0	+
22	15	45	8.0	0.10	Over 30 min	120	30	7.0	+
23	15	45	8.0	0.10	Over 60 min	120	30	7.0	+
24	15	45	8.0	0.10	Over 90 min	120	30	7.0	+
25	15	45	8.0	0.10	Over 120 min	120	30	7.0	+
26	15	30 (1:2)	8.0	0.10	All at a time	120	30	7.0	+
27	15	35.5 (1:2.5)	8.0	0.10	All at a time	120	30	7.0	+
28	15	45 (1:3)	8.0	0.10	All at a time	120	30	7.0	+
29	15	52.5 (1:3.5)	8.0	0.10	All at a time	120	30	7.0	+
30	15	37.5	8.0	0.10	All at a time	120	25	7.0	+
31	15	37.5	8.0	0.10	All at a time	120	30	7.0	+
32	15	37.5	8.0	0.10	All at a time	120	35	7.0	+
33	15	37.5	8.0	0.10	All at a time	120	30	7.0	+
34	15	37.5	8.0	0.10	All at a time	120	25	6.5	+

[a]—indicates no catalyst added; + indicates catalyst added in the amount mentioned above.

Study of film-forming property

The capacity of oxidised starch for forming a flexible gel film was reported by Boruch (1985). Gum-arabic-substituted modified starches can also be prepared by oxidation (Schmorak *et al.*, 1961). Based on these two ideas, starch films were prepared at three concentrations (20%, 25% and 30%) on a casting plate made of glass, as shown in Fig. 1. The casting plate was made by pasting a microscopy glass slide on a smooth surfaced glass plate with an adhesive. The blocks on the casting plate were of identical measurement. Solutions were prepared for all the sets of starches in test tubes at 98°C. Visual appearance, the texture observed visually, and the ease of making the solution, i.e. the time required to make the solution, were the basis of the selection of the best film in each case.

Glycerol is reported to assist in film formation (Boruch, 1985) hence glycerol was tried at 10 and 20%, based on the weight of starch, but was found to be not effective at 10%. At 20% it gave a sticky and transparent film. However, the time required to make the solutions was reduced considerably in the presence of glycerol.

The films thus obtained were graded arbitrarily for comparative purposes on a scale of 1 to 5 as follows:

1very flexible2flexible, but cracked3partly flexible, partly brittle4brittle5very brittle

RESULTS AND DISCUSSION

In the present work, a comparative effect of the process parameters on the oxidation of corn and amaranth starch was studied. Different parameters such as pH of the reaction, sodium hypochlorite concentration and mode of addition, time and temperature of the reaction, effect of catalyst on the reaction, starch:water ratio and final pH were changed as shown in Tables 1 and 2. The process was followed in terms of yield of the product and film-forming ability as well as some analytical criteria such as chlorine consumption, ferricyanide number and carboxyl content, the results of which are shown in Table 3.

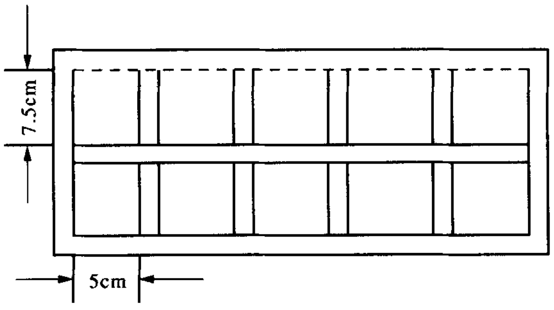


Fig. 1. Diagram of casting plate showing the dimensions of each section.

The pH of the reaction medium is known to play a vital role in the oxidation process. For instance, with wheat starch, the rate of oxidation is reported to decrease with an increase in pH from 7 to 10, and thereafter to remain constant up to at least 11.7. Similarly, studies on amylopectin oxidation with hypochlorite have shown the reaction rate to be highest at pH 7.0, a little lower at pH 5.5 and 9.0, and lowest at pH 11.0 and above (Patel *et al.*, 1974). Although the rate of oxidation is highest at pH 7.0, the rate of decomposition of the oxidant is also highest at pH 7.0, as it is converted to inactive chlorate (Floor *et al.*, 1989a). An increase in carboxyl content and a decrease in aldehyde content have also been reported with ascending pH (Hullinger & Whistler, 1951). The principal reaction products, i.e. glyoxalic acid and D-erythronic acid, are obtained in maximum yield at pH 7.0 (Patel *et al.*, 1974).

In the present work, in case of corn starch the yield ranged from 75.16 to 78.48% in the reaction pH range 7–9 taken for the study, the maximum being at pH 8.5. With amaranth starch, a maximum yield of 82% at pH 7.0 was observed, above which there was a decline in the yield.

Chlorine consumption was found to be maximum at pH 7.5 for corn starch while it reached saturation at pH 8.0 for amaranth starch. Carboxyl content, which is an indication of the extent of oxidation, was found to reach a maximum of 2.05% at pH 7.5 for corn starch while for amaranth starch a maximum of 0.75% was reached at pH 7.0 (Table 3). Ferricyanide number, an indication of the reducing value, also decreased as the pH was raised from 7.0 to 9.0 for both corn and amaranth starch. The film-forming ability was found to be greatest at pH 7.5 for corn starch and at pH 8.0 for amaranth starch (Table 4).

The effect of sodium hypochlorite concentration and its mode of addition on the oxidation of corn and amaranth starch is shown in Table 3, and the yield and film-forming ability are given in Tables 5 and 6. It was observed that as the sodium hypochlorite concentration increased, the chlorine consumption gradually increased from 0.15 to 1.87 over a range of 0.0256–0.25 g/g starch for amaranth starch and from 0.43 to 2.43 over a range of 0.05–0.25 g/g starch for corn starch. The extent of increase in ferricyanide number was very high for amaranth starch (3.5 to 29.8) as compared to corn starch (7.6 to 15.8). This could probably be attributed to a greater availability of the oxidised group in waxy amaranth starch. The yields decreased as the sodium hypochlorite concentration increased for both corn and amaranth starch. The film-forming ability was also dependent on concentration of NaOCl added, the best film being obtained at 0.15 g/g

Table 3. The effect of different parameters on the oxidation of corn and amaranth starch[a,b,c,d]

Trial no.	Variable parameters	Chlorine consumption		Carboxyl content (%)		Ferricyanide number	
		Corn starch	Amaranth starch	Corn starch	Amaranth starch	Corn starch	Amaranth starch
	pH						
1	7.0	0.045 (0.15)	0.306 (0.10)	1.8	0.75	18.11	18.41
2	7.5	0.063 (0.15)	0.031 (0.10)	2.05	0.47	12.99	15.16
3	8.0	0.058 (0.15)	0.032 (0.10)	1.67	0.56	14.51	10.39
4	8.5	0.047 (0.15)	0.032 (0.10)	1.93	0.56	12.13	9.53
5	9.0	0.047 (0.15)	0.032 (0.10)	1.84	0.37	7.58	6.93
	NaOCl concentration (g/g of starch)						
6	0.025		0.0026	—	0.15	—	3.51
7	0.05	0.006	0.0076	0.435	0.28	7.58	11.42
8	0.10	0.023	0.027	1.59	0.47	13.62	22.77
9	0.15	0.045	0.046	2.00	1.31	14.00	27.24
10	0.20	0.087	0.069	2.21	1.59	13.45	29.87
11	0.25	0.198	0.105	2.42	1.87	15.81	26.36
	Time (min)						
12	60	—	0.027 (0.10)	—	0.37	—	19.97
13	90	0.037 (0.15)	0.028 (0.10)	1.86	0.47	14.51	12.67
14	120	0.041 (0.15)	0.029 (0.10)	1.96	0.47	14.62	20.36
15	150	0.46 (0.15)	0.030 (0.10)	1.82	0.87	13.86	16.03
	Catalyst time (min)						
16	60	0.058 (0.15)	0.029 (0.10)	2.07	0.51	15.81	12.13
17	90	0.055 (0.15)	0.027 (0.10)	2.03	0.51	13.97	11.69
18	120	0.052 (0.15)	0.026 (0.10)	2.03	0.47	13.21	12.56
19	150	—	0.032 (0.10)	—	0.66	—	12.56
	No catalyst						
20	120	0.038 (0.15)	—	2.18	—	13.10	—
	No catalyst						
21	150	—	0.030 (0.10)	—	0.66	—	12.56
	S:W[d]						
22	1:2	—	0.035 (0.10)	—	0.63	—	12.25
23	1:2.5	0.049 (0.15)	0.034 (0.10)	2.07	0.59	16.81	12.90
24	1:3	0.046 (0.15)	0.030 (0.10)	2.07	0.55	15.38	12.47
25	1:3:5	0.045 (0.15)	0.0345 (0.10)	2.16	0.59	16.68	12.03
26	1:4	0.042 (0.15)	—	2.225	—	13.43	—
	Mode of addtion of NaCl						
27	All at a time	0.0275 (0.15)	0.031 (0.10)	2.05	0.56	18.89	13.56
28	Over 30 min	0.039 (0.15)	0.032 (0.10)	2.09	0.66	20.65	11.70
29	Over 60 min	0.031 (0.15)	0.031 (0.10)	2.30	0.12	19.55	10.96
30	Over 90 min	0.046 (0.15)	0.031 (0.10)	2.05	0.10	15.85	9.53
31	Over 120 min	0.017 (0.15)	0.027 (0.10)	2.05	0.56	21.31	11.2628
	Temperature (°C)						
32	25	0.046 (0.15)	0.0345 (0.10)	1.775	0.31	20.32	9.63

33	30	0.046 (0.15)	0.034 (0.10)	2.036	0.62	14.81	14.00
34	35	0.039 (0.15)	0.036 (0.10)	1.890	0.17	15.38	8.75
	pH						
35	7.0	0.045 (0.15)	0.034 (0.10)	2.03	0.59	15.01	14.51
36	6.5	0.044 (0.15)	0.034 (0.10)	2.04	0.53	14.62	15.32

[a] All the results are the average of two experiments.

[b] Values in parentheses indicate the concentration of NaOCl used in the oxidation process.

[c] The conditions of the experiments are as given in Tables 1 and 2.

[d] —indicates that set was not done.

[e] S:W = starch:water ratio.

starch for corn and 0.10 g/g starch for amaranth starch. For corn starch, the best films were obtained when NaOCl was added over a time span of 90 min whereas for amaranth starch addition all at one time gave best results. There are no comparable data on these aspects. However, it seems that the enhancement in the extent and rate of oxidation by increasing the NaOCl concentration (0.025 to 0.25 g/g starch) could be associated with greater availability of the hypochlorite/hypochlorous acid molecule. These results are shown in Table 7. It can be seen that the compact amylopectin-containing starch structure of amaranth starch does show a difference and therefore addition of oxidant at a faster rate gives the best film-forming ability.

Oxidised starches of higher viscosity and transparency could be obtained by use of inorganic catalysts such as $MgCl_2$, $CuSO_4$ and $NiSO_4$, as shown in some patented literature (Mehta & Mehta, 1966). A linear relationship between the carboxyl content and total mineral content is also reported (Ali & Kempf, 1986). For this reason the effect of $MgCl_2$ as catalyst was studied at 0.0115 g/g starch with both corn and amaranth starch. It was observed that with corn starch catalyst addition resulted in brittle films, whereas with amaranth starch the best film was obtained with catalyst addition over a period of 2 h (Table 7). For amaranth starch, addition of catalyst gradually increased the carboxyl content and the increase continued with the addition of catalyst during the 2 h reaction period. Table 8 shows the effect of reaction time on the yield and film-forming ability of corn and amaranth starch. It can be seen that the yield does not seem to be significantly affected by time.

The energy of activation of the oxidation reaction is shown to be low at pH 8.0 than with pH 10, within the temperature range of 27–37-47°C. In the present work, over a temperature range of 25–35°C the temperature effect was found to be insignificant for corn starch, although at a temperature of 25°C the ferricyanide number was high, carboxyl content was low and the yields were high. These reactions denote that at higher temperature the reaction is drastic, which is favourable for film formation. For amaranth starch carboxyl content and ferricyanide number were highest at 30°C, which gave a film that was flexible in nature.

The effect of starch concentration on the rate of oxidation of starch has been studied by Patel *et al.* (1974) and Schmorak *et al.* (1961). Their work indicated that the rate of oxidation increases linearly with starch concentration. In the present work, carboxyl content increased and the chlorine consumption decreased with decreasing concentration of corn starch. However, for amaranth starch no distinct effect was found on varying the starch concentration. The film was found to be more flexible at a starch:water ratio of 1:2.5. Adjustment of the final pH to 6.5 and 7.0 with 2 N sodium bisulphite was done

Table 4. Effect of pH on the yield and film-forming ability of oxidised corn and amaranth starch[a]

pH	Yield (%)		Film-forming property[b]	
	Corn starch	Amaranth starch	Corn starch	Amaranth starch
7.0	76.16	82.00	3	4
7.5	75.16	76.26	3[c]	4
8.0	77.76	76.53	4	3
8.5	78.48	75.60	5	4
9.0	78.20	78.33	5	4

[a] Other parameters are according to trials 1 to 5 in Table 3.

[b] Scored as follows for film character: 1, very flexible; 2, flexible, but cracked; 3, partly flexible, partly brittle; 4, brittle; 5, very brittle.

[c] Preferred due to lower decomposition of NaOCl.

Table 5. Effect of NaOCl concentration on the yield and film-forming ability of corn and amaranth starch[a]

NaOCl concentration (g/g of starch)	Yield (%)		Flim forming propery[b]	
	Corn starch	Amaranth starch	Corn starch	Amaranth starch
0.025	—	91.33	3	4
0.05	94.96	85.33	3	4
0.10	82.56	80.00	3	2
0.15	75.28	73.33	2	3
0.20	48.24	41.33	4	nd
0.25	35.52	31.33	4	nd

[a] Other parameters are according to trials 6 to 11 in Table 3.

[b] Scored as in Table 4.nd = not done due to very poor yields.

Table 6. Effect of mode of addition of NaOCl on the yield and film-forming ability of oxidised corn and amaranth starch[a]

Mode of addition of NaOCl	Yield (%)		Film-forming property[b]	
	Corn starch	Amaranth starch	Corn starch	Amaranth starch
All at a time	78.00	76.66	3	1
Over 30 min	78.60	75.60	3	2
Over 60 min	75.48	78.33	3	5
Over 90 min	77.28	79.33	1	4
Over 120 min	82.04	76.33	4	4

[a] Other parameters are according to trials 27 to 31 in Table 3.

[b] Scored as in Table 4.

Table 7. Effect of catalyst on the yield and film-forming ability of corn and amaranth starch[a]

	Yield (%)		Film-forming property[c]	
Catalyst + time of reaction[b]	Corn starch	Amaranth starch	Corn starch	Amaranth starch
Catalyst + 60 min	75.2	74.9	4	3
Catalyst + 90 min	74.7	76.6	4	3
Catalyst + 120 min	79.1	77.8	4	1
Catalyst + 150 min		72.6	4	2
No catalyst + 120 min	76.4		4	2
No catalyst + 150 min		78.8		

[a] Other parameters were according to trials 16 to 22 in Table 3.

[b] $MgCl_2$ was used as catalyst at a concentration of 0.0115 g/g starch.

[c] Scored as in Table 4.

with the aim of quenching the residual hypochlorite to some extent.

The above results yielded flow diagrams for oxidised starch preparation from corn and amaranth starch, which are shown in Fig. 2, a and b.

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Table 8. Effect of the time of reaction on the yield and film-forming ability of corn and amaranth starch[a]

Time of reaction	Yield (%)		Film-forming ability[b]	
	Corn starch	Amaranth starch	Corn starch	Amaranth starch
60 min	—	79.84	3	3
90 min	77.16	78.25	3	3
120 min	76.32	78.66	1[c]	3
150 min	82.44	77.53	1	1

[a] Without the addition of the catalyst. Other parameters are according to trials 12 to 15 in Table 3.
[b] Scored as in Table 4.
[c] Preferred due to lower time of solubilization.

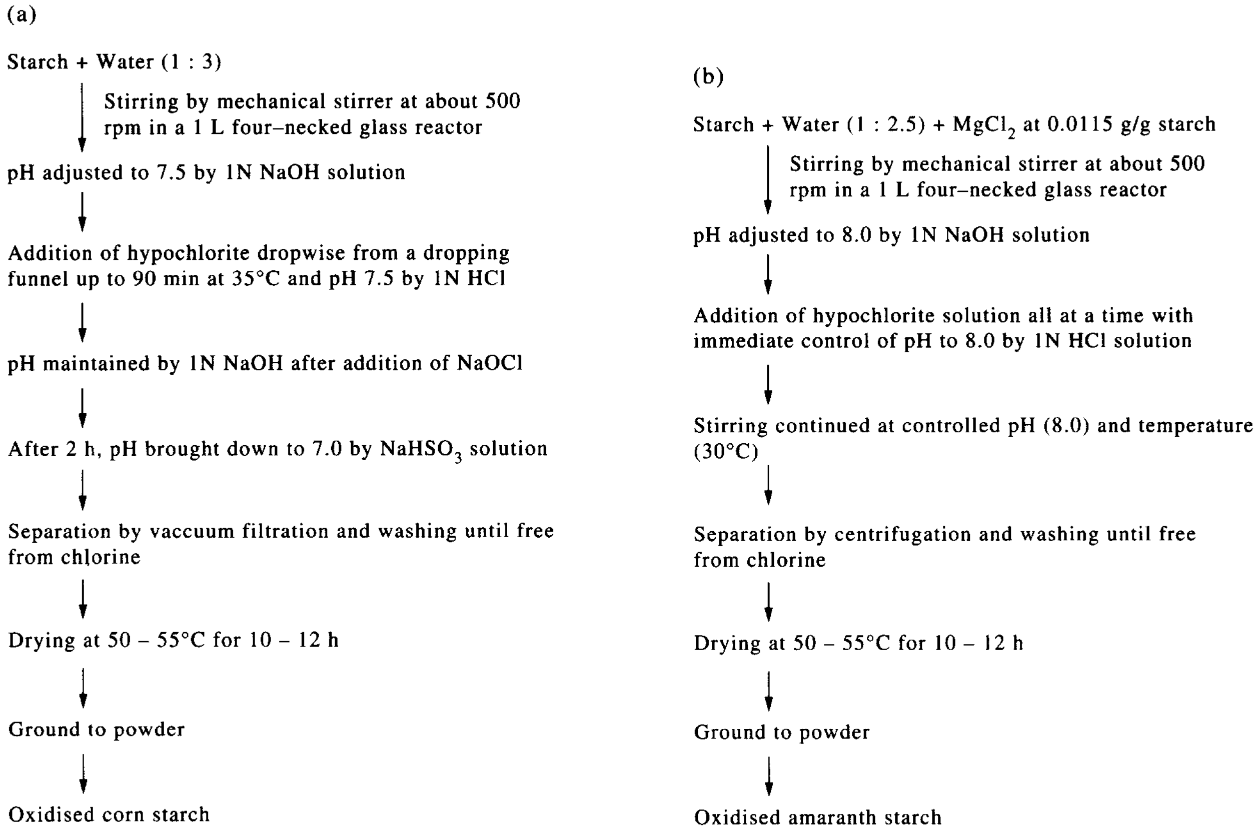

Fig. 2. (a) Flow sheet for the oxidation of corn starch; (b) flow sheet for the oxidation of amaranth starch.

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