A C T A A L I M E N T A R I A P O L O N I C A
Vol. VII (XXXI), No. 1-2 1981

TERESA FORTUNA
MIECZYSŁAW PAŁASIŃSKI

CHANGES IN THE PHYSICO-CHEMICAL PROPERTIES OF CATION STARCHES DURING AGEING *), **)

Department of General Chemistry and Food Technology Agriculture University, Kraków

Key words: ageing of starch, release of inorganic phosphate, changes in depolymerization, paste consistency, X-ray analysis of starch granules

Cation starches (H-, Na-, Ca-starch) which were stored during 18 years were studied for changes in depolymerization, release of inorganic phosphate, paste consistency, orientation of their crystalline structure and morphology of granules. The results obtained indicate that ageing is accompanied by a decomposition of glycosidic linkages, ester linkages of phosphoric acid and changes of the rheological properties of starch paste. The biggest changes were observed in the case of hydrogen starch, whereas sodium and potassium starches underwent comparatively small changes.

INTRODUCTION

The notion of ageing of starch granules covers the whole complex of physical and chemical changes occuring during long storage of these granules in a dry state, in standard laboratory conditions or in stores [7]. The first to write on this subject was Bielicki [1] who observed a considerable reduction of the potato starch paste viscosity during the ageing of starch. On the other hand, Niewiadomski [6] observed that also starch pastes are subject to ageing. Next, attention was drawn to the release of inorganic phosphate [2, 20] and to the chemical changes taking place in a starch molecule [14]. Extensive studies of the changes taking place in potato starch during long storage were conducted by Schierbaum

*) This paper has been presented to the international symposium on "Fundamental Studies of the Chemistry of Starch" held in Bratislava (1979).

**) The study was subsiddized by the Committee of Food Chemistry and Technology Polish Academy of Sciences.

[15, 16]. This author confirmed the opinions of other researchers concerning the processes of decomposition of glycoside and ester linkages in starch and changes in the rheological properties of their pastes.

In order to speed up the processes occuring during ageing, some authors used a higher temperature, e.g. 40°C [12] or heated starch with various water content levels (10%, 20%, 40% water) up to 50°C or even 100°C [17]. The keeping of starch preparations in a higher temperature is called artificial ageing. The B-spectrum X-ray analysis of potato starch treated in this way passes into the A-spectrum typical for grain starch.

An important role in these changes seems to be played by phosphoric acid that is chemically bound with potato starch as it determines a number of its physico-chemical properties the most important of which are its ion-exchange, autohydrolytic and rheological properties. The ion-exchange properties of potato starch have become a subject of study not so long ago [23]. These properties may be utilized to obtain cation starches because of the fact that amylophoric acid has two free hydroxyl groups whose hydrogen atoms have an exchange capability depending on the conditions of the environment. Amylophosphates obtained in this way have various properties depending on the type of cation bound with Starch "D" was used to receive the following cation starches:

There are very few data [12, 17] on the subject of ageing of cation starches. For this reason it seems appropriate to study the changes undergone by selected physico-chemical properties of potato starch saturated with various cations during prolonged storage.

MATERIAL AND METHODS

Potato starches stored for 18 years in laboratory conditions (in paraffin-coated jars at room temperature) were used for the studies. These starches were extracted in 1959 from five varieties of potatoes [9]:

1. "Capella" — a very late, high-starch variety,
2. "Deser" — a very late, low-starch variety,
3. "Cesarska Korona" — an early, low-starch variety,
4. "Lenino" — a very late, low-starch variety,
5. "Gromadzkie" — a medium-late, medium-starch variety.

The starches differened substantially in terms of total phosphorus content (57-108 mg% P).

Starch was obtained from each potato sample by laboratory methods
a) using distilled water according to Winkler [21] — starch "D",
b) using municipal water — starch "W".

Starch "D" was used to receive the following cation starches:
hydrogen (H-starches) — according to Winkler [22],

sodium (Na-starches) — according to Pałasiński [10],
potassium (K-starches) — according to Pałasiński [10],
calcium (Ca-starches) — according to Winkler (modified) [11]

In order to obtain comparable results, the same analytical methods used to test these starches 18 years ago were applied [8]:

— determination of dry substance was carried out by means of drying the starch sample at 130°C during one hour [3],

— inorganic phosphate content was determined by colorimetric method according to Marsh [4],

— the relative viscosity of aqueous starch paste 0.25% was determined on a capillary Ostwald viscometer [19].

In addition, the following analyses were carried out in order to better characterize the changes which took place during the ageing of cation starches:

— the reduction capacity of alkaline starch solutions was determined by Meyer method [5] using 3,5-dinitrosalicylic acid as modified by Richter [13],

— the gelatinization temperature range was determined with a "Betius" polarization microscope with a heating stage [13],

— the gelatinization characteristic was determined on the basis of Winkler's method [24] on a "Rheotest 2" rotation viscometer,

— the chromatographic elution analysis [13, 18] on filter paper was used to analyse starch fractions and the products of their desintegration qualitatively colouring with iodine.

Besides, some cation starches were submitted to X-ray examination in order to study their crystalline structure and examined under a scanning microscope in order to determine the morphology of starch granules.

RESULTS AND DISCUSSION

The results obtained are presented in Tables 1 to 3 and in Fig. 1 to 4. With a view to give a review of the changes observed during the ageing of starches of various origins (obtained from different potato varieties), Table 1 presents the mean values of the results obtained with a simultaneous indication of the fluctuations of particular determinations. The data in the Table 1 show that a release of inorganic phosphate can be observed in all starches after an 18-year period of ageing. This phenomenon is mostly recorded in starches extracted by means of distilled water (D-starch), to a lesser extent in hydrogen starches (H-starch) and starches extracted by means of minicipal water (W-starch). On the other hand, small amounts of inorganic phosphate were found in calcium starches (Ca-starch), sodium starches (Na-starch) and mainly in potassium starches (K-starch). The respective relationship can be clearly seen in Table 2

Table 1. A characteristic of starch after 18-year ageing (mean values)

Symbol	Content		Reduced viscosity ($cm^3 \cdot g^{-1}$)	Range of gelatinization temperature °C
	Inorganic P (mg P per 100 g d.s.)	Reduction capacity — % glucose		
D-Starch	7.8 (5.7-9.3)	0.24 (0.22-0.29)	182 (140-240)	61-74.5
W-Starch	4.0 (2.9-5.2)	0.25 (0.21-0.29)	239 (228-252)	60-73
H-Starch	4·9 (4.1-6.6)	9.09 (8.31-10.97)	8	60-71
Na-Starch	1.5 (0.7-3.0)	0.26 (0.22-0.33)	575.2 (400-780)	57-71
K-Starch	0.8 (0.5-1.6)	0.27 (0.22-0.31)	501.6 (332-760)	57-71
Ca-Starch	2.5 (1.8-4.7)	0.27 (0.23-0.30)	316.8 (228-444)	59-73.5

which presents the amount of inorganic phosphate in proportion to total phosphorus. This fact can be explained by the occurrence in starches incompletely saturated with metallic cation, of intermolecular hydrogen bridges which speed up the degradation of starch molecules.

The reduction capacity of starch after 18-year storage does not display any noticeable changes with the only exception of hydrogen starches where a huge increase of the reduction capacity is observed. The remaining starches show a reduction capacity similar to that of fresh starch.

In relation to the reduction capacity which, in a sense, characterizes the depolimerization level of the starches under test, quantitative data

Table 2. Inorganic phosphate released during the 18-year period of starch ageing

Symbol	Content		
	Inorganic P (mg P per 100 g d.s.)	P — total (mg P per 100 g d.s.)	Inorganic P in % from P-total
D_1	5.7	66.7	8.6
D_2	8.9	68.8	12.9
D_5	7.3	54.3	13.4
D_6	9.3	73.3	12.7
W_1	3.0	63.7	4.7
W_2	2.9	67.5	4.3
W_5	4.8	58.9	8.2
W_6	5.2	76.2	6.8
H_1	4.7	66.7	7.0
H_2	4.5	68.8	6.5
H_3	6.6	108.5	6.1
H_5	4.1	54.3	7.6
H_6	4.5	73.3	6.1
Na_1	1.2	66.7	1.8
Na_2	1.2	68.8	1.7
Na_3	3.0	108.5	2.8
Na_5	0.7	54.3	1.3
Na_6	1.5	73.3	2.0
K_1	0.5	66.7	0.8
K_2	0.8	68.8	1.2
K_3	1.6	108.5	1.5
K_5	0.6	54.3	1.1
K_6	0.7	73.3	1.0
Ca_1	1.8	66.7	2.7
Ca_2	2.0	68.8	2.9
Ca_3	4.7	108.5	4.3
Ca_5	1.9	54.3	3.5
Ca_6	1.9	73.3	2.6

were supplemented by the results of elution analysis of filter paper (Fig. 1). The chromatograms of hydrogen starch stored for 18 years were the only to display clear hydrolytic changes pointing to the depolimerization of this starch. The remaining starches showed hardly noticeable changes caused by a hydrolysis of starch preparations during the 18-year period of storage.

The greatest differences have been observed in the reduced viscosity of starch paste. In terms of viscosity, the types of starches under test may be listed as follows: Na-starch > K-starch > Ca-starch > W-starch > D-starch > H-starch. The highest viscosity continues to be observed in sodium starch followed by potassium starch, the lowest — in hydrogen starch.

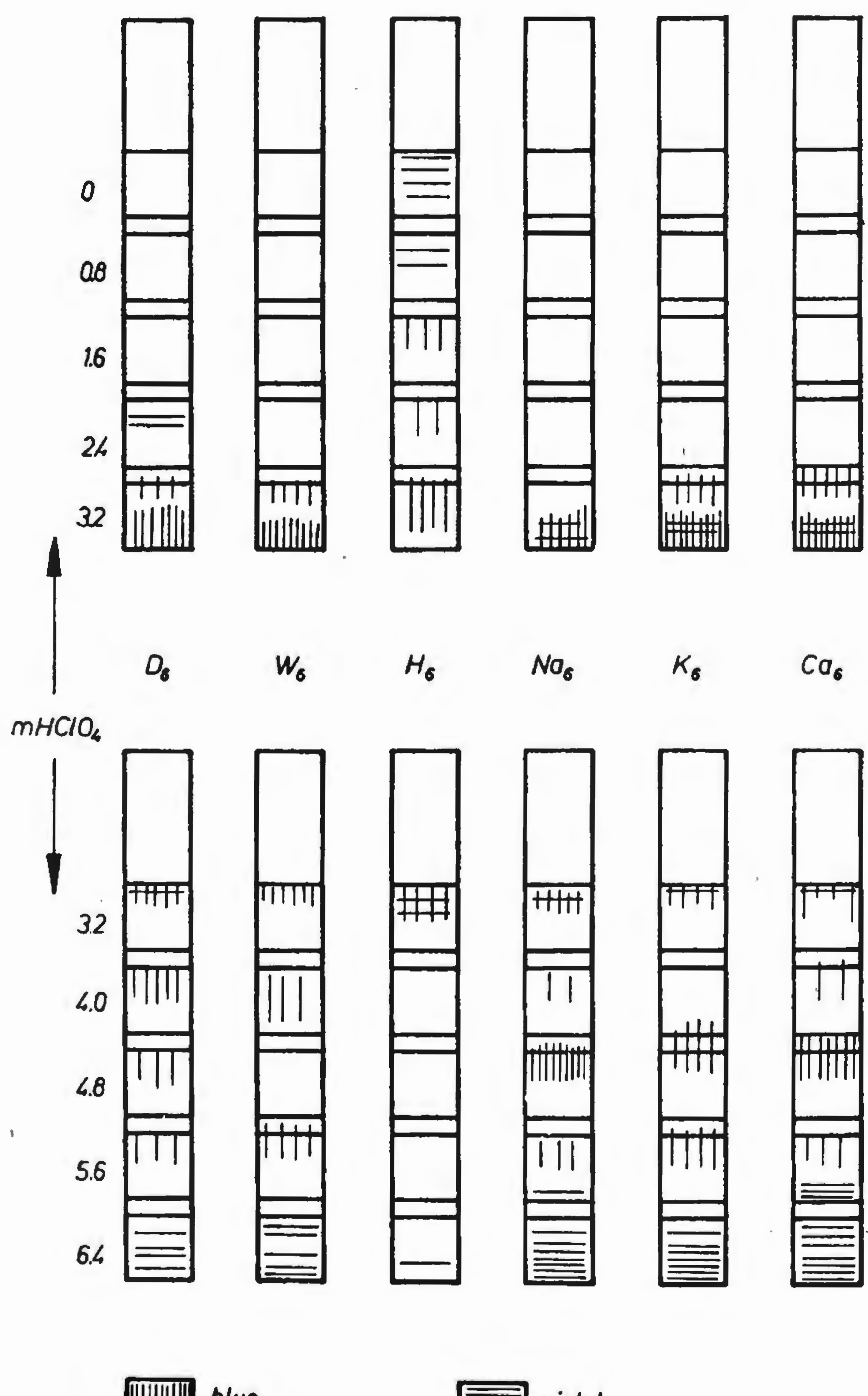

Fig. 1. A diagram of the chromatograms of the elution analysis of starch ("Gromadzkie" variety) after 18-year storage

The gelatinization temperature range after 18-year storage has been insignificantly shifted upwards as compared with fresh starch. The gelatinization characteristic of some starches was established by means of a "Rheotest 2" rotation viscometer. As shown by Fig. 2 the highest maximum of viscosity has been shown by sodium and potassium starch and definitely the lowest by starches extracted by means of distilled or municipal water. The temperature at maximum viscosity amounts to 75°C to 92°C. Cation starches are characterized by the highest temperature at maximum viscosity. Selected cation starches were submitted to X-ray examinations. Fig. 3 presents the diffractograms of initial and cation starches. For comparison sake, the diffractograms of particular starches were shifted in relation to each other and compared with a diffractograms of fresh starch (KW). The preparations studied do not show

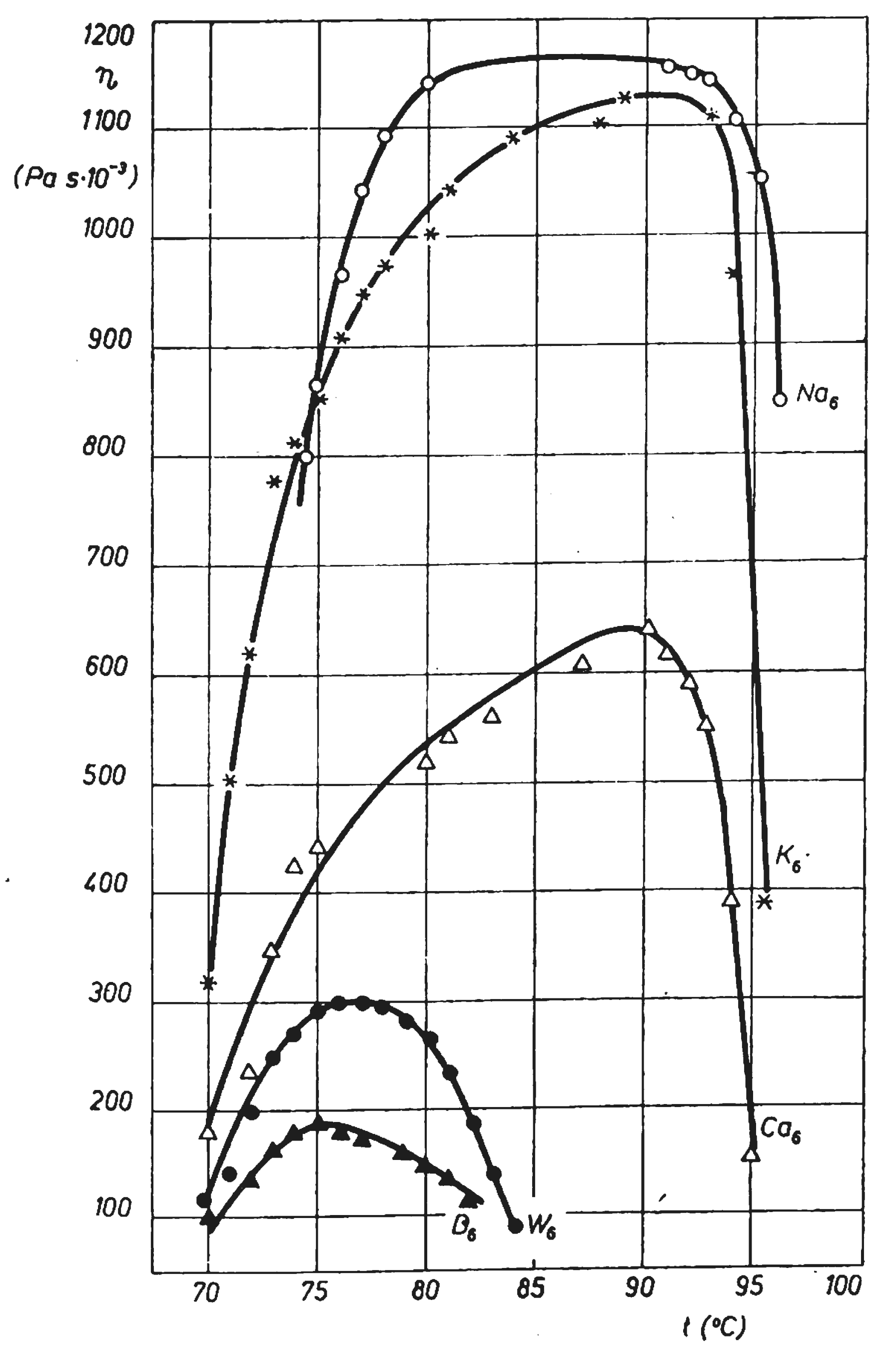

Fig. 2. A characteristic of the gelanization of starch ("Gromadzkie" variety) stored during 18 years, determined on a Rheotest 2 viscometer

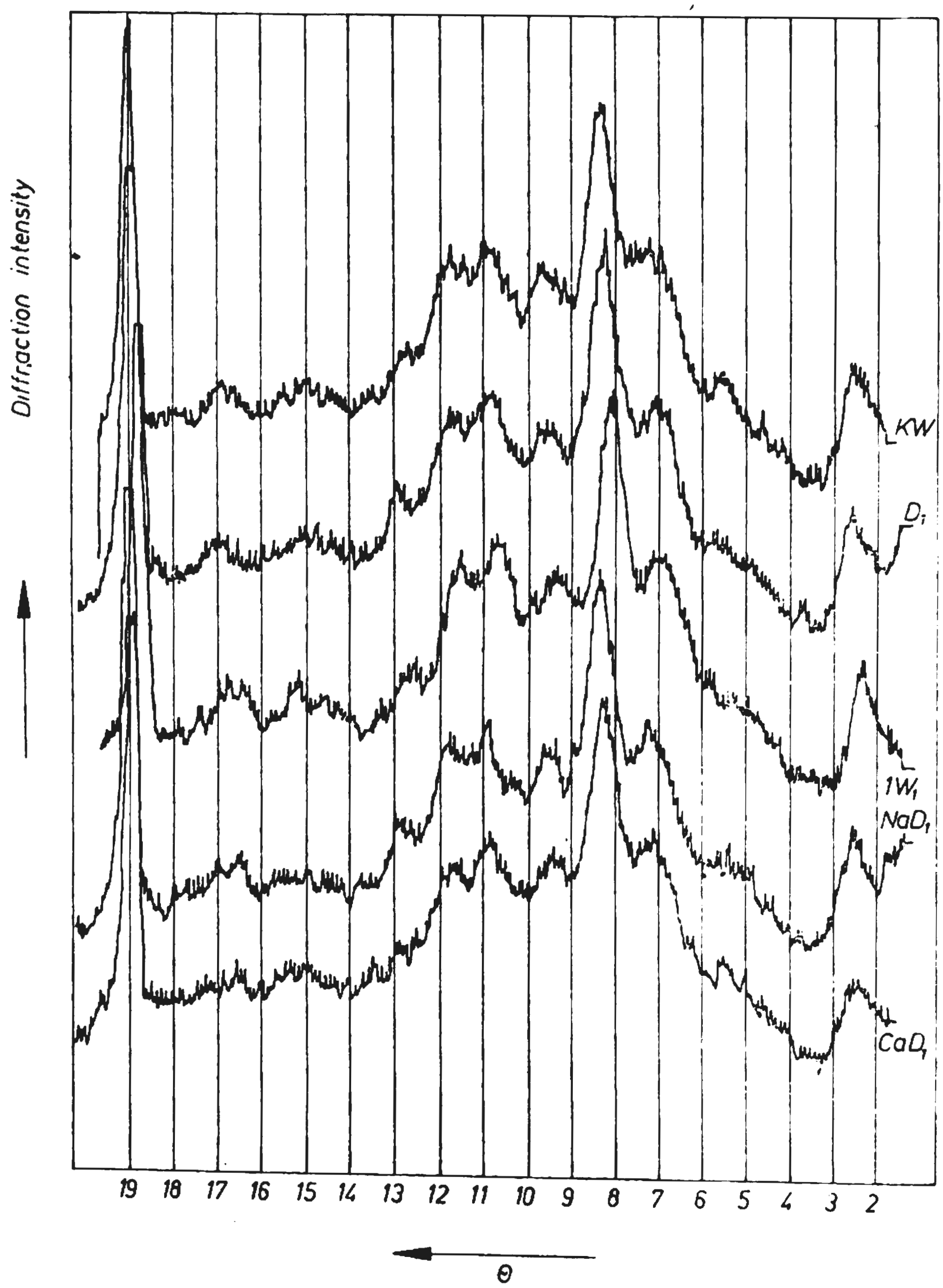

Fig. 3. Diffractograms of starch — diffraction intensity

Table 3. The value of the crystallinity level of cation starches extracted from "Capella" variety potatoes (of 1959)

No.	Symbol	Type of starch	Crystallinity level in %
1	Na_1	Na-Starch	30.7
2	Ca_1	Ca-Starch	30.6
3	D_1	Starch extracted with distilled water	31.9
4	W_1	Starch extracted with municipal water	31.4
5	KW	Industrial, fresh starch	29.9

any differences in crystalline structure which is confirmed by the data concerning the crystallinity level of the starches under test included in Table 3. Pictures made with a scanning microscope, listed in Fig. 4 made it possible to detect differences in the morphology of granules studied after an 18-year period of ageing. These microphotographs show that preparations isolated by means of distilled and municipal water have a surface as smooth as fresh starch whereas certain damages pointing to a small "corrosion" of the granules occur on the surface of cation starch granules. More pronounced changes of the surface of granules were observed in sodium and hydrogen starches.

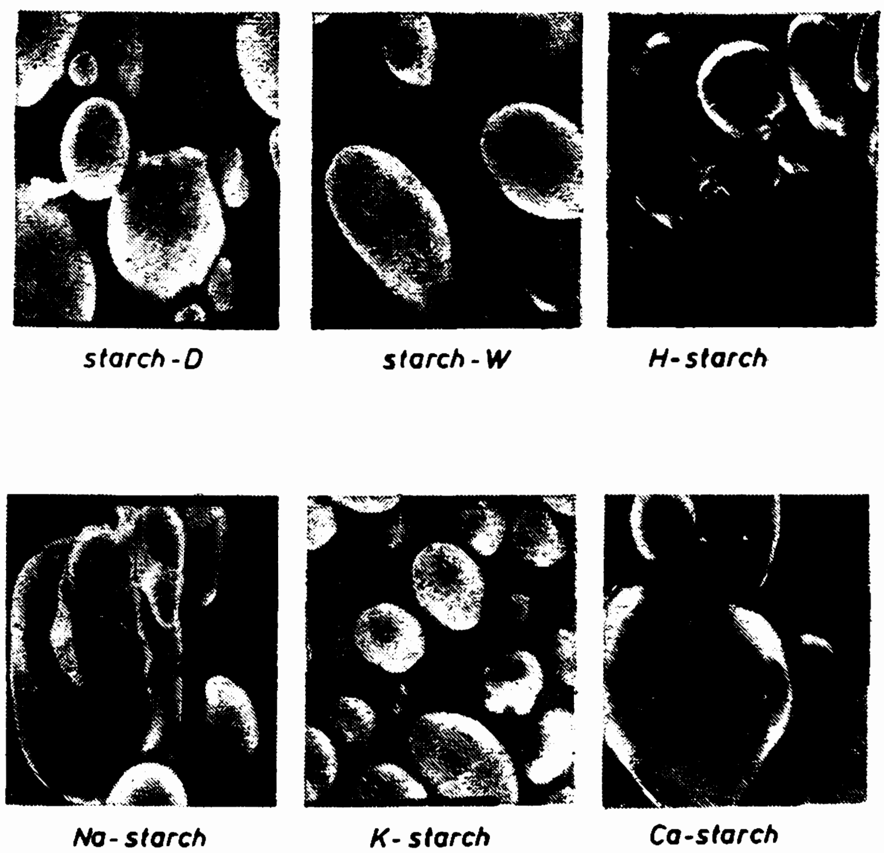

Fig. 4. Microphotographs of cation starch granules ("Capella" variety) made with a scanning microscope (1000x)

CONCLUSIONS

The results obtained make it possible to state that changes defined as "ageing" take place during a prolonged storage of cation starches. These changes are as follows:

1) a decomposition of amylophosphoric acid during which inorganic phosphate is released from starch. The intensity of this process depends on the type of cation which saturates the amylophosphoric acid,

2) depolimerization changes which take place in hydrogen starches. They have the character of a hydrolysis i.e. the decomposition of glycosidic linkages takes place under the influence of the hydrogen ions of starch itself. No hydrolytic decomposition was found in the remaining

cation starches during ageing; this is confirmed by the results of the elution analysis and the determination of reduction capacity,

3) a decrease of paste viscosity which takes place in all cation starches; sodium starch continues to have the highest viscosity,

4) an increase in gelatinization temperature and a shift of maximum viscosity to a higher temperature. The growth of gelatinization temperature is directly proportional to the amount of phosphate released during the process. Through a change of potato starch into sodium or potassium starch (Na-, K-starches) a high-viscosity preparation is obtained which, in addition, is less susceptible to the negative changes produced by ageing during storage.

It has been found on the basis of X-ray examinations that no changes in the crystalline structure take place during the ageing of starch granules.

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Manuscript received: March 1980
Authors address: 30-059 Kraków, al. Mickiewicza 24/28

T. Fortuna, M. Pałasiński

ZMIANY WŁAŚCIWOŚCI FIZYKO-CHEMICZNYCH SKROBI KATIONOWYCH PODCZAS STARZENIA SIĘ

Instytut Podstaw Chemii i Tec nologii Żywności AR, Kraków

Streszczenie

Krochmal ziemniaczany w trakcie magazynowania podlega przemianom określonym terminem starzenia się, w których pogarsza się jego jakość, a przede wszystkim następuje spadek lepkości kleików. W niniejszej pracy zbadano skrobie wyosobnione sposobem laboratoryjnym z różnych odmian ziemniaków przechowywanych przez 18 lat. Skrobie te różniły się między sobą zawartością kwasu fosforowego (od 56 do 108 mg P/100 g s.s.) oraz rodzajem kationu wysycającego kwas amylofosforowy (H-, Na-, K-, Ca-skrobie).

Skrobie przebadano pod względem stopnia rozłożenia polisacharydu (redukcyjność i analiza elucyjna), ilości uwolnionego kwasu fosforowego, charakterystyki kleikowania (temperatura kleikowania, lepkość zredukowana), stopnia uporządkowania struktury krystalicznej przy zastosowaniu analizy rentgenograficznej (tab. 3 i rys. 3) oraz morfologii ziarn skrobiowych przy użyciu mikroskopu skaningowego (rys. 4).

Uzyskane wyniki wykazują, że podczas starzenia się skrobi ziemniaczanej zachodzą procesy hydrolizy wiązań glikozydowych (tab. 1 i rys. 1), rozkładu estrowych wiązań kwasu fosforowego (tab. 2) oraz zmiany właściwości reologicznych kleików skrobiowych (tab. 1 i rys. 2). Największym przemianom ulega skrobia wodorowa, natomiast skrobie sodowa i potasowa zmieniają się stosunkowo w niewielkim stopniu i zachowują nadal najwyższą lepkość ze wszystkich przebadanych skrobi.

Zmieniając krochmal ziemniaczany w skrobię sodową lub potasową (Na- lub K-skrobię) otrzymuje się preparat nie tylko o wysokiej lepkości, ale również podatny w mniejszym stopniu na niekorzystne zmiany w wyniku starzenia się podczas przechowywania.