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# STARCH FORMULATIONS CONTAINING ELEMENTAL SULFUR

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Key words: encapsulation in starch, starch formulations of biological activity, sulfur suspensions in starch.

Potato starch formulations were prepared with elemental sulfur. Sulfur was added to starch paste in form of zole, as the colloidal solid or it was precipitated from ammonium polysulfide inside the paste. The amount of sulfur being suspended, its nature and the properties of formulations obtained depend on the preparation conditions. The formulations are characterized by the elemental analysis, pasting temperature, IR absorption spectra and powder X-ray diffraction.

## INTRODUCTION

Starch is known to form suspensions with sulfur. This property as well as formulations obtained have found some applications. Thus, starch can be used for defrothing sulfur concentrates [1]. Sulfur suspended in starch is proposed for the use as an anticryptogam [2]. Moreover such suspensions are used for manufacturing hydrogen sulfide either by fermentation [3] or pyrolysis [4].

We have payed our attention to the title formulations as potential drugs useful in dermatology as well as for curing some plant diseases, particularly these of the bark of trees. More extended studies are lacking on all suitable conditions of the preparation of suspensions, their stability and some physical as well as physico-chemical properties. This circumstance prompted us to study preparation methods of sulfur suspensions of various concentration in starch including different sources of colloidal sulfur. The form of sulfur suspended in starch has also been investigated

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by the powder X-ray diffraction. The kind of interaction between sulfur and starch are suggested based on the solid IR spectra of suspensions.

## EXPERIMENTAL

### STARCH FORMULATIONS WITH ELEMENTAL SULFUR

1. Zole of elemental sulfur was prepared from the mixture of sodium sulfide nonahydrate (6.4 g) and sodium sulfite heptahydrate (7.2 g) according to Gałecki [5, page 670]. This zole was added while stirring to the paste of potato starch "Niechlów" (36.46% C and 7.38% H) (5 g) in water (200 cm$^3$) at 62-65°C. Different amounts of sulfur zole were added in two subsequent preparations. Each of 100 and 200 cm$^3$ of the zole corresponded to attempted formation of 15% (Sample I) and 30% (Sample II) sulfur suspensions in starch, respectively. After the addition of the sulfur zole was over the stirring was continued for 1 h at the same temperature then allowed to stand for cooling to the room temperature. Precipitated material was separated on a centrifuge and either dried in the air or subject to dialysis followed by the air drying.

All the formulations form scale materials. This resulting from attempted higher concentration of sulfur and nondialyzed is particularly hard and stable in boiling water. Samples prepared form pastes in water at 70-75°C and all of them develop dark green colour with iodine. This colour turns dark blue after boiling reaction mixture. Dialyzed materials were analyzed for the content of carbon, hydrogen and sulfur. The pasting temperatures on the polarization microscope [6] are 80°C in both cases. Elemental analysis:

Sample I — C, 37.60%; H, 7.48%; S, 2.60%;
Sample II — C, 36,70%; H, 7.77%; S, 1.24%.

2. Colloidal sulfur was prepared from sodium thiosulfate nonahydrate [7]. Sulfur in the solid state was added to the paste of starch "Niechlów" (5 g) in water (200 cm$^3$). All 0.5 g, 1.25 g and 1.7 g of sulfur added corresponded to attempted preparation of 10% (Sample III), 25% (Sample IV) and 34.5% (Sample V) sulfur suspensions, respectively. The suspensions precipitated while cooling were subject to dialysis followed by separation on centrifuge and air drying.
Elemental analysis:

Sample III — C, 34.90%; H, 6.45%; S, 3.43%;
Sample IV — C, 34.81%; H, 6.64%; S, 8.95%;
Sample V — C, 37.42%; H, 7.81%; S, 1.38%.

The formulations undergo evident fractionation while precipitation as confirmed in the case of Sample IV. The fractions on the bottom (Sample

IVa) are enriched in sulfur in comparison with the fraction residing on the top (Sample IVb) of precipitated material.
Elemental analysis:

Sample IVa — S, 10.18%;
Sample IVb — S, 7.73%.

The formulations III to V form pastes in water at 80, 80, and 70°C, respectively and develop dark green colour with iodine which turns dark blue after boiling. The pasting temperatures on the polarization microscope [6] are 70, 75 and 70°C, respectively.

3. Ammonium polysulfide [5, page 87] (25 cm$^3$, 50 cm$^3$ and 70 cm$^3$ in subsequent experiments) was added to the starch paste made of starch "Niechlów" (5 g) in water (200 cm$^3$) to give Samples VI, VII and VIII of attempted sulfur content of 20%, 35% and 50%, respectively. The mixture of the paste with ammonium polysulfide was stirred for 15 min. then neutralized with diluted aq. sulfuric acid. Precipitated yellow solid was separated on centrifuge, washed with water and dried in the air without preceding dialysis.
Elemental analysis:

Sample VI — C, 22.99%; H, 6.26%; N, traces, S, 18.85%;
Sample VII — C, 23.68%; H, 5.15%; N, traces, S, 34.19%;
Sample VIII — C, 20.84%; H, 4.68%; N, traces, S, 46,30%.

Samples form pastes in water at 85, 85 and 95°C, respectively and develop dark green colour with iodine which turns into dark blue after boiling. The pasting temperatures on polarization microscope [6] are 80, 80 and 90°C, respectively.

## SPECTRAL MEASUREMENTS

Spectral measurements in the infrared region (400-650 cm$^{-1}$) were carried out in the KBr pellets by means of Specord 71 IR apparatus of Carl Zeiss Jena.

X-Ray powder diffractograms of the samples were recorded by means of the Debye-Scherrer camera d = 114.6 mm. The Cu $K_\alpha$ irradiation lasted 8.5 h at 30 kV and 20 mA.

## RESULTS AND DISCUSSION

Sulfur is well known for its bactericidal, fungicidal and parasiticidal properties. It can be applied either in form of vapours or as the additive to various formulations like, for instance, soaps. We consider sulfur on the starch support or encapsulated in the starch matrix to be biodegradable mixtures potentially useful in dermatology, as hygienic aids as well as formulations for curing some plant diseases.

The biological activity of the formulations attempted should depend on the size of sulfur particles and their amount suspended in starch. Moreover, any practical applicability depends on further factors like the mode of suspending sulfur in starch which can be either in form of sulfur adsorbed on the surface of starch or encapsulated within the starch matrix. All the stability, the ability to the formation of pastes, stiffness or hardness of the compositions should also be taken into account.

Two series of colloidal sulfur have been applied for the preparation of attempted formulations. The mixture of sodium sulfide and sodium sulfite delivered colloidal sulfur in form of zole which was added to aqueous starch paste. Precipitated composition forms very hard, insoluble nonpasting material, especially in the case of nondialyzed product. These properties predistinate this formulation to be suitable for curing diseases of the bark of trees. Dialysis of this composition rather significantly reduces its hardness. Less hard formulations are achieved when colloidal sulfur precipitated from sodium thiosulfate is suspended in a starch paste. The amounts of sulfur being added in every experiment was much higher than its amount found by the elemental analysis of resulting mixtures. Thus, in the case of the zole added 2.6 and 1.24% of sulfur were found in the final suspension instead of intended 15 and 10% of this element, respectively. Instead of compositions containing 10, 25 and 34.5% sulfur 3.43, 8.95 and 1.38% sulfur compositions with starch have been obtained, respectively, if the solid colloidal sulfur was added. These results point to the starch to have quite poor adsorptive and encapsulating properties in respect to colloidal sulfur. The majority of sulfur is removed in the mother liquor from the centrifuge. Since a part of sulfur formed from both its sources does not have the colloidal form the decomposition of these salts with acids in the starch pastes has been postponed.

The formulations of high sulfur content can be achieved when ammonium polysulfide is decomposed by sulfuric acid within the starch paste. Almost whole the polysulfide sulfur introduced resides in the final compositions. However, it should be noted that only part on the sulfur precipitated from this source forms colloidal zoles. High content of sulfur in starch makes these formulations much easier to mechanical disintegration.

The method of the preparation of the compositions determines also their more subtle properties like interactions between sulfur particles and glucose units of the starch. It is illustrated by their ir absorption spectra presented in Fig.

Spectrum of potato starch itself (2) very closely resembles in the region of 2000-1300 cm$^{-1}$ the spectrum of colloidal sulfur (1). Therefore, the

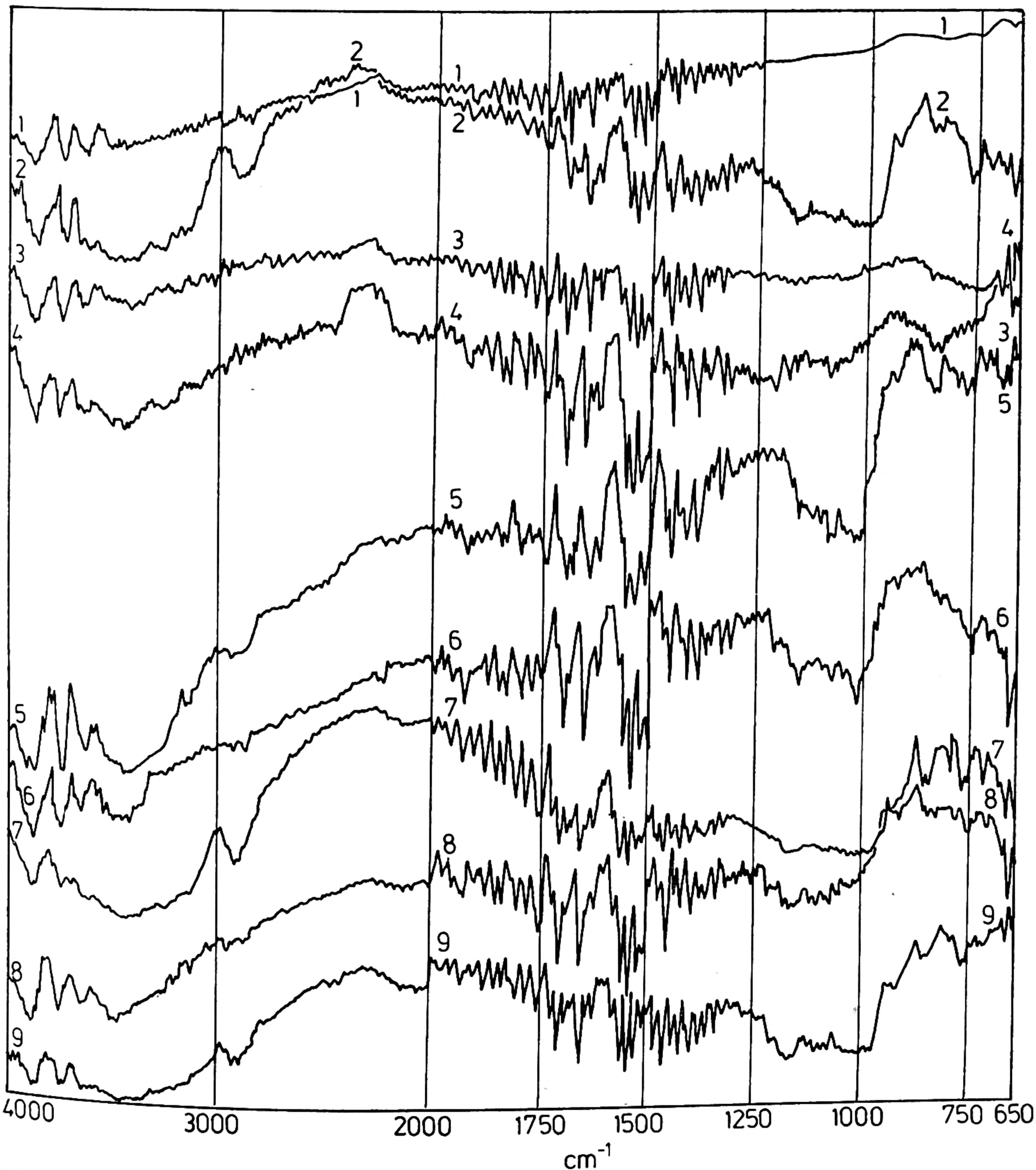

Fig. The IR absorption spectra (in KBr) of: 1 — colloidal sulfur, 2 — untreated potato starch, 3 — Sample I, 4 — Sample II, 5 — Sample VI, 6 — Sample VII, 7 — Sample III, **8 — Sample III**, 8 — Sample IV, 9 — Sample V

pattern of this region does not change in the spectra of all formulations prepared. Most essential spectral changes occur in the regions of 3600-2700 and 1300-1200 $cm^{-1}$. There is in the spectrum of starch a broad intense band centered at 3450 $cm^{-1}$ related to OH stretching vibrations, the band of medium intensity at 2900 $cm^{-1}$ due to CH stretching modes and a broad intense band between 1300-1200 $cm^{-1}$ which consists of overlaped deformation modes of CH, C-O-C and $OPO_3H$ moieties of the structure of starch. The addition of sulfur even in a relatively small amount but in form of zole produces essential changes in the spectrum of starch in both latest regions. Thus, these bands almost entirely cease. It is well observed in the spectrum of Sample I. This fact should not be accounted for masking peaks of starch by sulfur. The spectra containing much more sulfur exhibit quite intense maxima under discussion. Therefore, some specific sulfur — starch interactions have to be taken into account in the case of starch treated with zole of colloidal sulfur. The results of further procedures seem to document coagulating activity of starch against colloidal sulfur. It is confirmed by the investigation of the degree of crystallinity of the samples carried out by the powder X-ray diffraction measurements (Table).

The specificity of Samples I and II deduced from the IR absorption spectra is nicely supported by the powder X-ray diffractograms.

Both original potato starch as well as colloidal sulfur exhibit their own diffraction pattern. The analysis [8] of diffractogram of colloidal sulfur prepared from sodium thiosulfate shows that it is submicrocrystalline orthorhombic alothropic form. Samples III, IV and V show diffraction pattern which is composed of the overlapped diffractograms of both components of the suspension. This is not the case with Samples I and II. Apart from d-lines attributed to sulfur and to starch some other d-lines can be observed in the relevant diffractrograms. They confirm the presence of specific interactions between components of this formulations. The diffractograms of Samples VI, VII and VIII show the lines belonging solely to sulfur and the d-lines characteristic for starch are absent. It points to starch to turn into amorphous form under the influence of the preparation conditions.

## CONCLUSIONS

The formulation formed by the combination of aqueous starch paste and colloidal zole of sulfur from sodium sulfide and sodium sulfate presents a scale like hard material useful for curing diseases of the bark of tree.

Colloidal sulfur is rather poorely accepted by starch but it interacts specifically with starch matrix.

Formulations prepared by suspending pure colloidal sulfur and starch paste are real physical mixtures of both components. The yield of sulfur adsorbed is low.

Formulations of high content of sulfur are best prepared from starch paste and ammonium polysulfide mixture treated with sulfuric acid. They are also real physical mixture of sulfur and possibly partly hydrolyzed starch.

*T a b l e I. Diffraction pattern of potato starch, sulfur and sulfur containing starch formulations*

| No. | Starch | | Sulfur | | Sample[a] | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | I | | II | | III | | IVa | | IVb | | V | | VI | | VII | | VIII | |
| | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ | $I^b$ | $d_\alpha$ |
| 1 | | 5.95 | | 6.61 | | 5.72 | | 6.15 | | 5.72 | m | 5.68 | | 6.42 | | 6.25 | | 5.69 | | 6.37 | m | 5.73 |
| 2 | | 5.08 | m | 5.66 | m | 5.08 | | 5.70 | | 5.13 | m | 5.14 | | 5.73 | | 5.77 | | 4.31 | | 5.73 | | 4.25 |
| 3 | | 4.48 | m | 4.21 | | 4.07 | | 5.13 | | 4.40 | | 4.28 | m | 5.14 | s | 5.13 | s | 3.87 | | 5.13 | | 4.04 |
| 4 | m | 4.02 | | 3.99 | | 3.82 | | 4.49 | | 4.00 | | 4.06 | | 4.36 | | 4.46 | | 3.60 | | 4.23 | s | 3.82 |
| 5 | | 3.66 | s | 3.80 | | 3.19 | | 4.00 | | 3.66 | s | 3.83 | | 4.03 | | 4.08 | | 3.44 | | 4.04 | | 3.55 |
| 6 | | 3.36 | | 3.53 | | 3.05 | s | 3.87 | | 3.39 | | 3.67 | s | 3.84 | s | 3.88 | m | 3.21 | s | 3.85 | m | 3.45 |
| 7 | | 2.83 | m | 3.41 | | 1.86 | | 3.63 | | 3.13 | | 3.56 | | 3.47 | | 3.45 | m | 3.08 | m | 3.57 | | 3.31 |
| 8 | | 2.59 | | 3.29 | | 1.80 | | 3.45 | | 2.86 | m | 3.44 | m | 3.21 | | 3.33 | m | 2.83 | m | 3.43 | m | 3.20 |
| 9 | | 1.91 | m | 3.18 | | | | 3.34 | | 2.60 | | 3.34 | m | 3.08 | | 3.20 | | 2.61 | | 3.33 | m | 3.08 |
| 10 | | 1.87 | m | 3.07 | | | | 3.22 | | 1.86 | m | 3.21 | m | 2.83 | | 3.08 | | 2.48 | m | 3.20 | | 3.01 |
| 11 | | | | 2.82 | | | | 3.11 | | 1.82 | m | 3.07 | | 2.61 | | 2.83 | | 2.39 | m | 3.08 | | 2.60 |
| 12 | | | | 2.66 | | | | 2.86 | | | | 2.84 | | 2.48 | | 2.63 | | 2.27 | | 2.85 | | 2.49 |
| 13 | | | | 2.59 | | | | 2.60 | | | | 2.67 | | 2.42 | | 2.28 | | 2.10 | | 2.62 | | 2.42 |
| 14 | | | | 2.47 | | | | 1.86 | | | | 2.63 | | 2.28 | | 2.11 | | 1.89 | | 2.49 | | 2.35 |
| 15 | | | | 2.40 | | | | 1.82 | | | | 2.49 | | 2.10 | | 1.89 | | 1.83 | | 2.43 | | 2.28 |
| 16 | | | | 2.36 | | | | | | | | 2.42 | | 1.90 | | 1.83 | | 1.78 | | 2.37 | | 2.19 |
| 17 | | | | 2.28 | | | | | | | | 2.34 | | 1.84 | | 1.72 | | 1.72 | | 2.29 | | 2.10 |
| 18 | | | | 2.08 | | | | | | | | 2.28 | | 1.77 | | 1.69 | | 1.65 | | 2.11 | | 1.90 |
| 19 | | | | 1.89 | | | | | | | | 2.11 | | 1.72 | | 1.60 | | 1.45 | | 1.90 | | 1.82 |
| 20 | | | | 1.82 | | | | | | | | 1.90 | | 1.70 | | | | 1.41 | | 1.86 | | 1.77 |
| 21 | | | | 1.77 | | | | | | | | 1.82 | | 1.66 | | | | 1.35 | | 1.82 | | 1.72 |
| 22 | | | | 1.73 | | | | | | | | 1.77 | | 1.60 | | | | | | 1.78 | | 1.69 |
| 23 | | | | 1.71 | | | | | | | | 1.72 | | | | | | | | 1.75 | | 1.65 |
| 24 | | | | 1.69 | | | | | | | | | | | | | | | | 1.72 | | 1.61 |
| 25 | | | | 1.64 | | | | | | | | | | | | | | | | 1.69 | | |
| 26 | | | | 1.61 | | | | | | | | | | | | | | | | 1.63 | | |
| 27 | | | | 1.44 | | | | | | | | | | | | | | | | 1.60 | | |
| 28 | | | | 1.41 | | | | | | | | | | | | | | | | 1.55 | | |
| 29 | | | | 1.35 | | | | | | | | | | | | | | | | 1.42 | | |
| 30 | | | | | | | | | | | | | | | | | | | | 1.35 | | |

[a] For the notation of the samples see Experimental Part of this paper.

[b] s — strong, m — medium, if not denoted the $d_\alpha$ is weak.

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# PREPARATY SKROBIOWE ZAWIERAJĄCE ELEMENTARNĄ SIARKĘ

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## Streszczenie

Otrzymano preparaty skrobiowe zawierające elementarną siarkę. Siarkę dodawano do skrobi bądź pod postacią wodnego zolu bądź jako koloidalną siarkę w postaci stałej. Również wytrącano siarkę w kleiku skrobiowym zmieszanym z wielosiarczkiem amonowym przez zobojętnienie mieszaniny reakcyjnej. Ilość zawieszonej siarki, jej charakter oraz właściwości otrzymanych preparatów zależą od sposobu ich sporządzania. Doświadczenia przeprowadzone z koloidalną siarką dodawaną w formie zolu lub w postaci stałej świadczą, że skrobia wykazuje słabe właściwości adsorpcyjne i kapsułkujące względem koloidalnej siarki. Stąd tylko nieznaczne ilości siarki zostają osadzone w skrobi, a większość siarki wprowadzonej zostaje usunięta z ługami macierzystymi. Skrobia, która była skleikowana w momencie mieszania z siarką powraca po ochłodzeniu do stanu krystalicznego. Niemal całą dodaną siarkę udaje się utrzymać w skrobi, gdy siarkę strąca się z wielosiarczku amonowego w kleiku skrobiowym. Skrobia w takich preparatach pozostaje w formie bezpostaciowej.

Badania preparatów przeprowadzone metodami analizy absorpcyjnej w podczerwieni oraz proszkowej analizy rentgenowskiej świadczą, że w tych preparatach, które otrzymano przez mieszanie zolu siarki koloidalnej z kleikiem skrobiowym obserwuje się specyficzne oddziaływania pomiędzy składnikami mieszaniny. Dowodzi tego wygląd widma absorpcyjnego dla próbek I i II (rys. 1, widmo 3 i 4). Najwyraźniej widma te swym wyglądem w zakresach ok. 3500 i 1000-1250 $cm^{-1}$ odbiegają od widm pozostałych otrzymanych próbek. Specyficzności próbek I i II dowodzą też wyniki badań metodą proszkowej analizy rentgenowskiej, która (tabela) ujawnia w dyfraktogramach obecność takich linii $d_\alpha$, które nie należą ani do czystej siarki ani do czystej skrobi. Linii takich nie obserwuje się w dyfraktogramach pozostałych próbek.