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EVALUATION OF NEW TYPES SEQUESTERING AGENTS AND THEIR EFFECT ON THE MODEL WASHING OF TEXTILE MATERIALS

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A sequestering agent or a chelating agent are the substances capable of removing a metal ion from a solution system via formation of a complex ion that does not possess the reaction activity of the ion removed. These agents are being used to eliminate the water hardness and some metals, such as iron; both having found a wide applicability in the textile industry. The sequestration capacity was measured at 20 °C and 90 °C using media with different pH and in combination with precipitating opacity titration — the so-called Hampshire test. The samples were tested at model washing conditions after 20× repeated washing in hard water (22 °dH, for 30 min at 90 °C) to determine the content of the ash and Ca^{2+} ions. The image of fabric after such a model washing has then been evaluated with the aid of imaging with a scanning electron microscope.

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Introduction

Textile auxiliary agents may ease, speed up, improve, or even enable as such technological treatments and are, therefore, used in the production of textile, as well as in some finishing operations. Sequestrate agents represent one of the most significant groups of these (textile) auxiliary agents.

These substances are most frequently used as a component of detergents; then, for textile finishing; being applicable also otherwise, e.g., like dyeing cellulose materials or as effective water softeners.

A textile production is dependent on the quality of water, which is a vital raw material used not only for the boilers that supply steam for heating and drying, but also for all the wet processes — boiling, bleaching, dyeing, printing, and finishing. Thus, it is obvious that good water quality is the basic precondition for textile plants.

There is well-known adverse effect of alkaline earth ions (Ca^{2+}, Mg^{2+}), causing the water hardness during various processes of the textile industry. An important property of sequestrates is the ability to suppress the precipitation of $CaCO_3$. This slightly soluble compound is being deposited at higher temperatures as a water stone, thus affecting the functioning of various devices, their temperature regime, etc. Besides, $CaCO_3$ can also be deposited on the treated textile, which now has a rough handle. The hard water may lower the efficiency of textile auxiliary agents and the proper run of the other textile finishing processes.

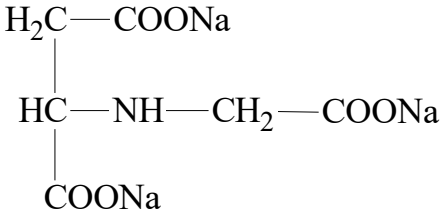
In general, sequestrates are the compounds that are able of forming chelates, thus offering a specific kind of complex-forming reagents for common cations, such as Ca^{2+}, Mg^{2+}, Fe^{3+}, Cu^{2+}, or Mn^{2+}. (In the respective structures, the metallic cation is the central atom being strongly locked by other inversely charged ions or even obscured by a neutral molecule.)

Nowadays, several types of sequestering agents are in use, namely: polyphosphates, aminopolycarboxylates, hydroxycarboxylates, polyaminophosphonate and polyhydroxyphosphonate, or polymeric carboxylic acids [1]. As known, traditional chelating agents do not decompose readily in the environment. Hence, there are increasing demands on cleanness of wastewater and the application of biodegradable washing components and/or finishing baths of textile productions leads to new knowledge about the recently used sequestrates. Typical new types of sequestrate agents are surveyed in the following points:

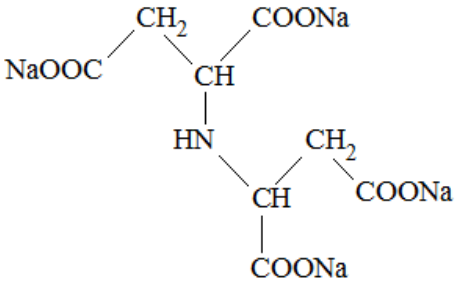
- Polycarboxylic compounds containing nitrogen (nitrilotriacetic acid [2], glutamic acid [3], aspartic acid and its derivates [4,5,6], agents based on imidodisuccinic acid, polyasparic acid, hydroxyethylimidoacetic acid [7,8])
- Copolymers of acrylic acid with monosaccharides or oligosaccharides [9]
- Copolymers of acrylic acid with vinyl acetate [10]
- Grafted polysaccharides [11]

Experimental

The Prepared Samples



Sample No. 1



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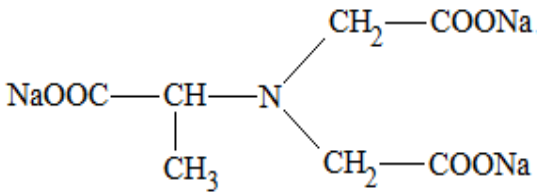

Trilon M (commercial sequestrate agent)

Evaluation of the Sequestration Capacity

The sequestration capacity was evaluated with model agents and compared to that of the commercially marketed sequestrate agent. Evaluation of the sequestration capacity was carried out for the Ca^{2+} ions when using precipitating opacity titration — the so-called Hampshire test [12], at two different temperatures of 20 °C and 90 °C. For the latter, a solution of sequestering agent was tempered at 90 °C and then titrated, when a solution of $CaCl_2.6H_2O$ had been selected as a volumetric solution. The equivalence point was determined *via* the respective absorbance of the opacity formed during the reaction that was measured at the wavelength of 650 nm in a glass cell (thickness: 1 cm). For this purpose, a spectrophotometer (model

Spekol 11; Carl Zeiss Jena, Germany) was used and the data obtained were consequently evaluated with the aid of a standard method of quantitative analysis.

The Sequestrate Agent Efficiencies at the Condition for Model Washing

Prepared agents were determined under conditions for model washing. The detergent chosen consisted of anion-active and non-ionogenic surfactant, and further common components, such as water glass (soln. of sodium metasilicate), carboxy-methylcellulose, sodium carbonate, and sodium sulphate [13]. The sequestrates determined were added into this basic mixture, when the washing filling had contained 7 g l^{-1} model washing agent. The washing material was then a portion of 20 grams of cotton textile, at a bath ratio of 1:20.

After 20× repeated washing in hard water of 22 °dH (given in German degrees of hardness) for 30 min at 90 °C, the content of ash and Ca^{2+} ion were determined. After 20× repeated washing, the textile was incinerated in a platinum crucible and the amount of calcium was evaluated in ash. The titration was accomplished with Chelaton III (13.270 g l^{-1}) according to the recommended procedure [14]. Finally, the image of fabric after the model washing was evaluated by means of images from a scanning electron microscope.

The Biodegradability

The biodegradability was evaluated for the sample No. 1 with the standard OECD (Paris 1981; Test Guideline 301D called „ Biodegradability – closed bottles procedure. Accredited process No. 308; SOP ET 8).

Results and Discussion

Tables I and II survey the values of the sequestration capacity for pH 11 and pH 12, when the parameter studied has depended on the increasing temperature and pH. It is possible to say that the sequestration efficiency decreases with the increasing temperature. The measured values obtained for prepared samples No. 1 and No. 2 at 20 °C are comparable with those declared for the commercial sequestrate agent Trilon M. As seen, the sequestering ability at 90 °C of the sample No. 1 is lower. Otherwise, the values of the sequestration capacity were as expected and given by the chemical structure of the samples where the content of functional groups enabling the sequestration is of primary importance.

Due to the fact that the significant part of the world production of the sequestrate agents is used for manufacturing of detergents and the cleaning agents,

Table I Values of the sequestration capacity at 20 ºC and 90 ºC for pH 11

Sample	Sequestration capacity, mg Ca^{2+} per gram of dry material	
	20 °C	90 °C
1	165.4	68.5
2	194.4	169.3
Trilon M	203.7	166.6

Table II Values of the sequestration capacity at 20 ºC and 90 ºC for pH 12

Sample	Sequestration capacity, mg Ca^{2+} per gram of dry material	
	20 °C	90 °C
1	173	52.5
2	142	113.4
Trilon M	197.5	154.2

the samples prepared were tested at model washing conditions. The washing with model detergent without sequestering ingredients increased the content of inorganic deposits in cotton textile. The content of ash and calcium in textile is relatively high: 3.18 % ash and 15.20 g Ca^{2+} kg^{-1}. The addition of prepared samples with sequestrate effect improved the result as documented by the data in Table III. The image of fabric after model washing was evaluated by means of images obtained with a scanning electron microscope — see Figs 1-3. With the addition of agent with sequestrate, the resultant effect was improved, which was the case of the commercial product, too.

Table III Content of ash and calcium ion in the cotton textile after twenty five times repeated washing in hard water 22 °dH

Sample	Ash content, % w/w	Content of Ca^{2+}, g kg^{-1}
1	0.50	1.76
2	0.08	0.08
Trilon M	0.06	0.43
Without prepared samples	3.18	15.20
Commercial washing agent	4.55	18.50

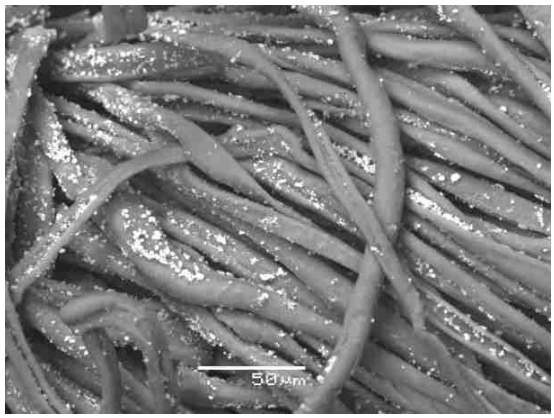

Fig. 1 Picture of the fibre surface of cotton textile washed without the sequestrate agent with model detergent (enlargement 500×)

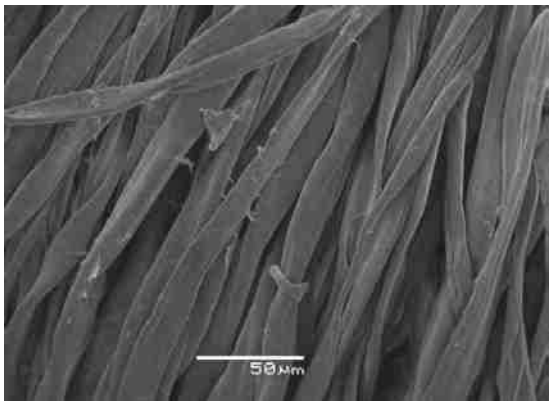

Fig. 2 Picture of the fibre surface of cotton textile washed with the sequestrate agent No. 2 (enlargement 500×)

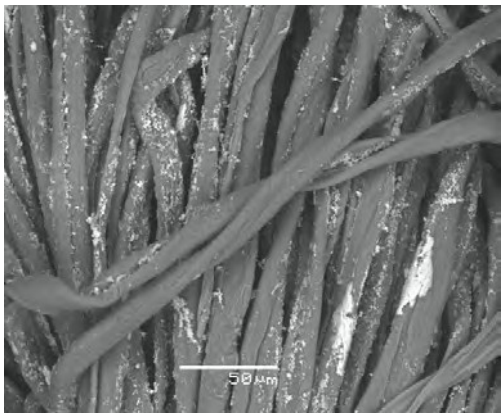

Fig. 3 Picture of the fibre surface of cotton textile washed with the commercial washing agent (enlargement 500×)

Conclusion

In this work, the basic properties of two prepared samples of sequestrate agents have been evaluated. By measuring the sequestering ability of the samples prepared, it has been found that respective value is comparable to that declared for the commercial product of Trilon® M. The positive effect of model sequestrates has then been confirmed at conditions of the model washing. An indisputable benefit of the sample prepared is good biodegradability (namely: 72.6 %), it means that it has exceeded 70 %, which is a limiting value specified by the E.U. standards.

It can be concluded that the sequestrate agents prepared are applicable in many detergent formulas and as the textile auxiliary agents for some finishing operations.

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