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A NOVEL APPROACH FOR SULPHUR TEST ON VISCOSE BASED MATERIALS

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ABSTRACT

When the fiber consumption rates are considered, consumption of viscose fibers is gradually increasing in connection with the increasing demand and trends. Regenerated fibers with cellulosic base and different properties are produced in order to fulfil every kind of need with the aid of new production techniques developed especially in the last years. However, certain problems are confronted in repeatibility in finishing processes because of the differences in production methods, and most of these problems are projected to be sourced from sulphur present on the viscose fabrics. In spite of all of these, there is no standard sulphur indication method in the market that is widely accepted. To determine the sulphur content, a practical test system for sulphur indication was developed and a sulphur scale like "TEGEWA Violet Scale" to evaluate the starch desizing degrees was formed in scope of this study. With the aid of this scale, the presence of sulphur on viscose and the amount can be determined practically, even though it is a subjective method.

Keywords: Viscose, sulphur, sulphur analysis, sulphur scale, finishing

INTRODUCTION

Wood cellulose is the most widely used raw material of manufactured fibers made from natural polymers. Fibers obtained by the regeneration of wood cellulose are named as "regenerated cellulose fibers" [1]. Rayon (artificial silk, viscose filament fiber, viscose rayon), which was produced to take the place of valuable silk, is the first regenerated cellulose fiber [2]. In 1892, Cross, Bevan in England and Beadle in USA has managed to solve the cellulose in the form that is not nitrocellulose as it was previously. Cellulose was processed with caustic soda and then with carbon disulphide, and viscose process, that is used presently, was discovered [3]. Production for commercial usage has been made by an American company Avtex Fibers in 1910. First rayon has been named as regenerated silk, however producers thought word regenerated was not a good commercial name. At last, "rayon" name was found. French word "rayon" means "rays of light," "light beams." In 1924, "rayon" has entered the industry as an official name. In the beginning, it couldn't take the place of silk, however rayon producers tried to improve the properties of these fibers, and these studies were made mostly in USA, Russia and Japan [2].

We cannot disregard that viscose method, used widely in the production of regenerated cellulose fibers, has drawbacks from the

viewpoint of ecology because of the emissions of CS_2 and H_2S. With the aim to solve this problem;

a) technological improvements
b) researches to develop new resolvents and new methods are intensively made.

As a result of research, Lyocell fibers are produced by dissolving the cellulose raw material in the solvent N-methylmorpholine –N-oxide (NMMO), which can be completely reclaimed after the process. Thus Lyocell fibers have a more ecological production method in comparison to the other regenerated cellulosic fibers [4]. However, viscose fibers cannot be neglected both from the viewpoint of costs and the effects they provide.

Because viscose fibers are regenerated fibers, a sub group of man-made fibers, they are naturally clean. So their pretreatment processes are not complex. However according to their origin, properties and the end use of viscose fibers, pretreatment processes can change. Unlike other regenerated cellulose fibers, macromolecular structure is very susceptible to the treatment processes [5]. Therefore any change during treatment processes can have directly effect on the fiber's physical and chemical properties. Sulphur residues may be present on some viscose fabrics as a result of the fiber production methods. During the spinning of viscose fibers CS_2 is used and after spinning in some cases sulphur residues can remain and these sulphur residues can cause problems such as color effeciency of prints done with reactive dyestuff, repeatability of the print, penetration to the back, uniformity of printing in treatment of viscose fibers [10, 11].

EXPERIMENTAL

A practical method (lead acetate method) for determination of sulphur content was detected from the several identification tests such as barium chloride, iodine solution, potassium permanganate and lead acetate. Among these methods, it was decided to use lead acetate method, and owing to the this method after a standardization and optimization, a sulphur scale was developed. [6,7]. During these studies, 17 different 100 % viscose woven fabrics in different structures and sulphur residues were used but especially the plain woven fabric having 98 g/m^2 weight was used for standardization of lead acetate method and for improving a sulphur scale.

During this test, H_2S was released from these elemental sulphur and sulphur salts existed in viscose fabrics by treatment with strong acid "HCl". It is a highly poisonous gas with a smell of rotten eggs. This gas dissolves in water forming a very weak acidic solution, from which salts known as sulphides (such as Na_2S, CaS) may be derived. In turn, many metals react directly with sulphur to form metal sulphides. The sulphides of heavy metals are all insoluble in water. Those of the Group IA and IIA are however soluble in water. The sulphides of lead, copper, and silver are black. Solutions of lead, silver or copper salts yield black precipitates when exposed to hydrogen sulphide [8].

$Pb(CH_3COO)_2 + H_2S$? $PbS + CH_3COOH$ [9]

All the chemicals used to standardize the sulphur analysis method and to obtain good repeatibility have analytic purity.

TABLE I.

Chemicals and laboratory equipments used in the sulphur analysis method and their purity

Lead acetate [$(CH_3COO)_2Pb.3H_2O$]	powder, (Merck)
Zinc (Zn)	powder (Merck)
Hydrochloric acid	% 37 (Merck)
Sodium sulphide	powder (Merck)
Sodium sulphate	powder (Merck)
Sodium disulfide	powder (Merck)
Sodium dithionate	powder (Merck)
Sodium thiosulphate	powder (Merck)
Filter paper	391 Grade, 80 g/m2 (Filtrak)
Beaker	100 ml
Erlenmeyer flask	100 ml (diameter of mouth = 20 mm)

Processes realized for the determination of sulphur on the viscose material are divided into two parts. In order to control the precision of lead acetate method and to find out relationship between the amount of sulphur on the material and the results, solutions of 1 g/lt from different sulphur compounds (sodium sulphide, sodium sulphate, sodium disulfide, sodium dithionate, sodium thiosulphate) were prepared. Then 10 different sulphur solutions of 1, 3, 5, 8, 10, 15, 20, 25, 30, 35 ml were taken from these solutions that are 1/100 diluted. After that, these solutions put into erlenmeyer flask and the volume is completed to 35 ml with water. Then, zinc powder, HCL (26%) of 5 ml were added respectively and erlenmayer flask was dwelled for 15 minutes after it was closed with a filter paper impregnated with lead acetate. Meanwhile zinc powder reacts with acid and as a result hydrogen gas and zinc chlorite, which is capable to solve viscose in acidic pH [12]. So the reaction of the sulphur residue found in the fiber with HCl and also the formation of H_2S was provided easily.

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)} \quad [13]$$

In the second part of the study, method was standardized and trials were realized with the viscose material. Also, sulphur analysis made on the viscose material was tested with the aid of sulphur determination on the CHNS elemental analysis device. As it was in the first part of the study, here also it was observed that color of the filter paper impregnated with lead acetate deepened as the amount of sulphur on the viscose material increased, and thus sulphur scale was developed in this way.

Afterwards, measurements with CHNS – 932 (LECO) Elemental Analysis Device were made to determine the sulphur content on the viscose fabrics used for the standards and to test the precision of the scale.

RESULTS AND DISCUSSION

Data obtained by testing compounds containing sulphur with lead acetate method

The principle of the method is to detect H_2S (hydrogen sulphide) gas released from the material so, the method avails when H_2S gas is formed otherwise no color change is observed on the filter paper. The sulphate forms of sulphur could not be measured, since H_2S (hydrogen sulfide) gas is formed very little to be observed or not formed at all. It was established that for the compounds giving color, color of the filter

paper deepens as the concentration of the compound increases. With the aim to observe the increase of K/S value of the color in line with the sulphur concentration-according to Kubelka Munk Theory-, Sodium thiosulphate solution was diluted 1% and 0.5 ml, 1 ml, 3 ml, 5 ml, 7ml, 10 ml, 13 ml, 15 ml, 20 ml were taken from the solution and water was added to those solutions until to the final volume of 25 ml, and filter papers were colored with the aid of sulphur analysis method mentioned above. Color efficiencies (K/S) of the colored filter paper were calculated, and following graphic is formed by examining the correlation between the sulphur amounts.

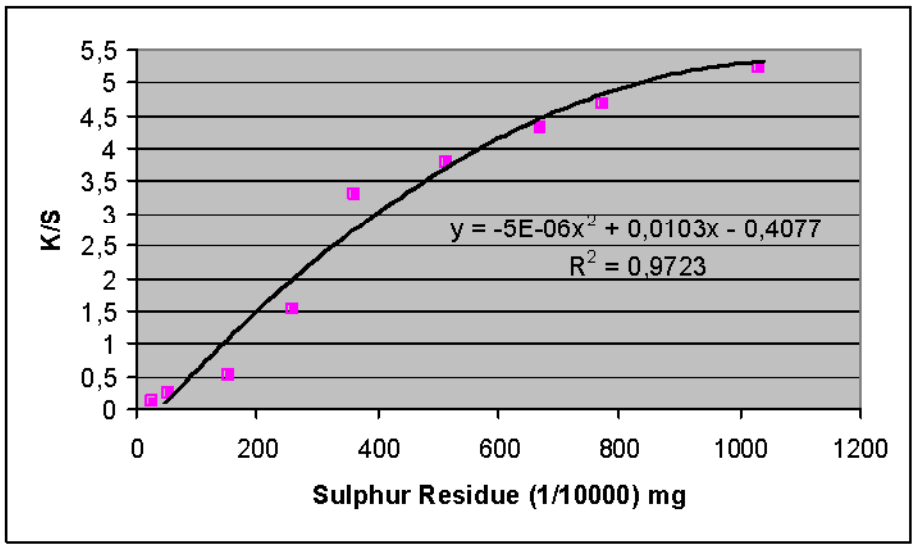


Fig. 1. The relationship between the color deepness of filter paper and the sulphur content of the solution.

R^2 values are high so the equation on the figure 1 characterizes the color efficiencies of the samples. Approximately 97% of values obtained from the samples provide a polynominal tendency.

Standardization of lead acetate method and sulphur scale

In contrast to the common belief that sulphur residues were removed during the viscose process, sulphur residues are still found in viscose fibers. For example, among the 17 different viscose fabrics, investigated in this study, 12 fabrics have sulphur residues in different amounts (Table II). Measuring the amount of the sulphur residues accurately, rapidly and in a repeatable way is yet another problem. In order to solve these problems, firstly a qualitative method was standardized and then a new sulphur scale (Figure 2) was developed with the aid of this novel method. During the experiments, sulphur scale grades (SSG) were determined by this method and scale.

TABLE II.

Viscose fabrics used in the study and the sulphur residues found on the fabrics

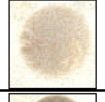
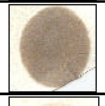
Woven type	Whiteness (Brightness)	Weight (g/m^2)	Yarn count		Fabric count		Results of test (Lead acetate method)
			Warp	Weft	Ends/cm	Picks/ cm	
Plain	63.26	108	40.26	40.76	23	26	
Twill 3/1	70.11	203	53.68	27.77	61	25	
Plain	62.43	124	37.57	41.66	30	26	
Plain	75.01	169	27.18	28.22	29	24	
Plain	65.69	173	29.23	29,54	29	25	
Plain	77.29	164	Ne 27.33	29.35	28	24	
Plain	76,63	116	45	25	35	28	
Plain	69,07	98	47	26	39	24	
Javanaise	64,51	98	41	24	38	23	
Georgette	54,01	83	39	37	32	25	
Plain	72,6	106,4	28	28	35	27	
Plain	61,1	155	38	38	44	27	
Marocain	70,94	160	44	19	40	21	
Satin	67,99	191,5	57	29	65	26	
Georgette	62,83	85	44	38	33	24	
Georgette	57,6	73	48	45	36	26	
Marocain	61,86	131	40	14	42	18	

TABLE III.

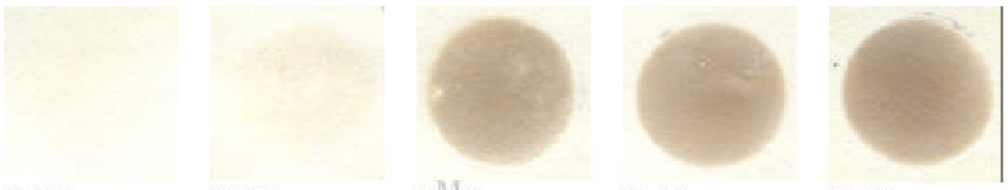
Step by step standardized sulphur analysis method

- Take a 0.5 g of sample
- Fill one 100 ml beaker with 20 ml hot water and then put the sample into it
- Add 0.3 g zinc powder into the beaker, mix it and wait for a minute
- Take the sample from the beaker and put it into 100 ml erlenmayer flask
- Pour 13 ml HCl (32%) into the erlenmayer flask
- Afterwards, cover the erlenmayer flask with filter paper impregnated with a lead acetate solution (25%) (In order to determine the sulphur amount in the sample precisely, erlenmayer flask has to be covered with the filter paper immediately)
- After 13 minutes, remove the filter paper and cover it with a film
- Match the color on filter paper with the standardized SSG

In order to improve the sulphur scale, plain woven fabric having 98 g/m^2 weight was treated with different pretreatment processes such as reductive washing, causticizing and bleaching and their combinations with each other(s). After these pretreatment processes, sulphur tests were managed with the use of lead acetate method and the results obtained from the lead acetate method were then checked with Elemental analysis equipment (table IV).

TABLE IV.

Measurement results obtained on the CHNS-932 (LECO) elemental analysis device.



% C	40,92	40,83	40,69	40,42	42,52
% H	6,79	7,79	6,99	6,49	8,23
% N	0,057	0,083	0,03	0,036	0,13
% S	0,016	0,018	0,027	0,038	0,064

When it was determined that results of elemental analysis and standardized lead acetate method are parallel to each other and color darkness of the filter paper increases in line with the amount of sulphur, L* a* b* values of colors on the filter papers were determined with the aid of X-RITE SP 78 Model Spectralphotometer, and scale was formed as it is shown in Table V by using these values and Adobe Photoshop 5.5.

TABLE V.

Color values of the sulphur scale grades

Color Value	L*	a*	b*	C	M	Y	K
*S.S.G. 1	93	-1	3	10	5	10	0
S.S.G. 2	84	1	10	17	16	24	1
S.S.G. 3	71	6	13	25	31	36	5
S.S.G. 4	61	5	9	35	36	40	11
S.S.G. 5	55	6	8	39	42	43	18

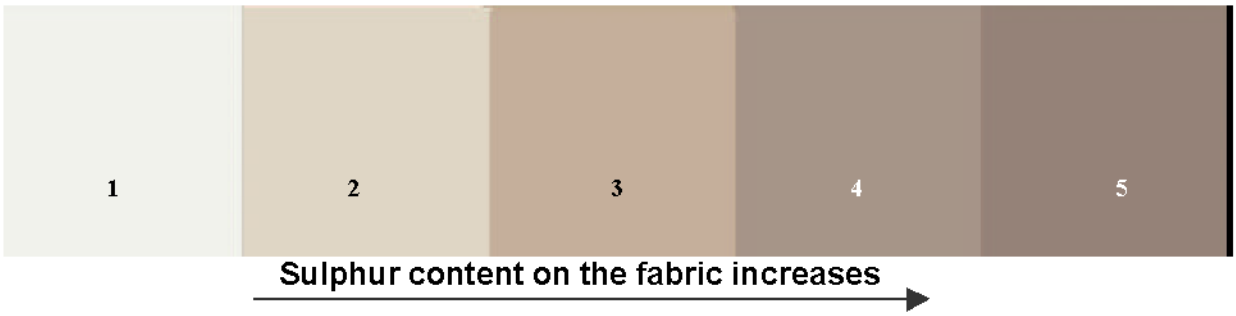


Fig. 2. Standard sulphur scale.

With the use of these properties, the hydrogen sulphide released from viscose fabric was detected with filter paper impregnated with lead acetate, then the color of filter paper was hydrogen sulphur gas matched with Standard Sulphur Scale.

CONCLUSION

Sulphur residues may be present on some viscose fabrics as a result of the fiber production methods. To determine the sulphur content, a practical test method which is developed by the authors, can be easily used in every plant like "TEGEWA Violet Scale" to evaluate the starch desizing degrees[14].

Various sulphur analysis methods were investigated and tested with the aim to determine the sulphur amount on viscose. Among these methods, lead acetate method, which is a subjective evaluation, is found to be the most appropriate one with regard to the practical working conditions in plants. As a result of the trials made, it was found that method is effective as long as hydrogen sulphur gas is released, and no color is observed in compounds containing sulphate, since formation of free sulphur is very little or none. But the repeatibility of this method was not good, since substance amounts used in the method (weight of the test sample, amount of zinc powder used, acid concentration and amount, water amount), processing times (dwelling time of the filter paper impregnated with lead acetate, for example wetting time) and the properties of the glass material used were not specified. In order to provide repeatibility and to obtain a homogeneous color on the filter paper, parameters expressed above were standardized and the method was reformed. Then, with the help of reformed standart method shown in table III, a scale named "sulphur scale" was developed and finally a more practical and universal technique for evaluation of the sulphur residues found in fibers was rectified.

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REFERENCES

1. Loy, W., Chemiefaserstoffe-Aufbau-Eigenschaften-Verwendung, Fachverlag Schiele & Schön GmbH, Germany, 1978, 29-35 p., 110-112 p, 119-124 p.
2. www.costumegallery.com/Textiles/rayon.htm, (04.15. 2004)
3. Gordon-Cook, J., Handbook of Textile Fibres, Shildon, Eng., Merrow Publishing Co., 1984,9-15 p.
4. Breier, R., Lenzinger Berichte, No.9, 1994, 99-101 p.
5. Smole M.S., Persin, Z., Kreze, T., Kleinschek K. S., Ribitsch, V., Neumayer, S., Materials Research Innovations, Vol. 7, No. 5, 2003, 275-282 p.
6. Bassett, J., Denney R.C., Jeffery G.H., Mendham, J., Vogel's Textbook of Quantitative Inorganic Analysis, Longman Scientific & Technical, Essex, 1987, 504-511 p.
7. Treadwell F.P., Hall T.W., Analytical Chemistry, Volume I, John Wiley & Sons. Inc. New York, 1956, 355-356 p.
8. http://www.physchem.co.za/Inorganic/Sulpur.htm (04.15. 2004)
9. Svehla, G., Vogel's Qualitative Inorganic Analysis,1996, Longman Group Limited, 63 p.
10. Özgüney, A. T., Tarakçioglu, I., Körlü, A.E., Özerdem, A., Bahtiyari, M. I., The Journal of the Textile Institute, Vol. 96, No. 5, 2005., 319-327 p.,
11. Tarakçioglu I., Özgüney A. T., Ekmekçi A.,Özerdem A., Bahtiyari M.I., World Textile Conference 4 th Autex Conference Roubaix FRANCE, 22-24 June 2004
12. http://www.chemguide.co.uk/physical/basicrates/concentration.html
13. http://www.science.siu.edu/chemistry/chem439/lab_fiber.html
14. Karmakar S. K., Chemical Technology in the Pre-Treatment Processes of Textiles, Elsevier, 1999, 451 p.