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**APPLICATION OF NEW TYPES
OF THE SEQUESTERING AGENTS TO COLOURISE
COTTON WITH THE REACTIVE DYES
IN HARD WATER**

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In this work, a possibility to use the sequestering agents in the development stage for colourising in hard water was investigated. To treat a cotton material in this way, the reactive dyes of vinylsulfone type were chosen. The quality of coloration was evaluated using the degree of exhaustion of the dye bath together with an objective color measurement.

Introduction

The cotton is by far the most commercially important plant. Its fibre structure exhibits up to 90-95 % cellulose, containing also pectins, proteins, fats, waxes,

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lignin, ashes, etc. Textile materials of natural cellulose character have to be thoroughly pre-treated prior to dyeing. Impurities as well as matter which adhere to the fibres during the previous treatments are being removed by desizing, alkaline scouring, and bleaching. The process of such a preparation imparts to the cotton yarn or cotton fabric a better appearance, increased strength and, mainly, easier colourability due to the singeing and mercerizing steps [1].

Reactive dyes have been very popular for dyeing and printing of cellulosic fibre for many years. These dyes are characterized by a high brilliance of hue, being also good or even excellent in fastness of the colourising process. They are suitable not only for natural and regenerated cellulose, but also for animal and synthetic (polyamide) fibres. Reactive dyes form a special group capable of forming a chemical bond with the cellulosic substrate, thus forming a dyestuff – fibre bond. During the dyeing, the reactive-atom groups or reactive atoms alone react with the primary –OH cellulose groups. Depending upon the type of reaction, the reactive dyes are divided into two large categories: (i) dyes reacting through the nucleophilic substitution and (ii) dyes undergoing the nucleophilic addition (like, e.g., vinylsulphone dyes) [2,3].

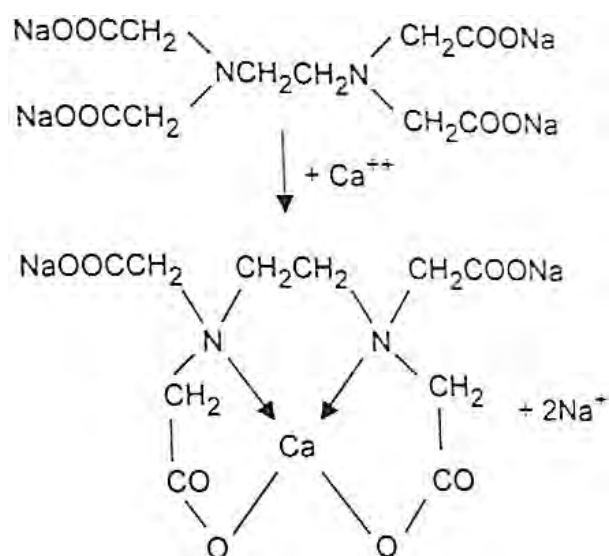


Fig. 1 Chelation of calcium ion with EDTA

In textile wet processes, the water quality is the most crucial parameter and the water itself is undoubtedly the most suitable dyeing medium. Otherwise speaking, the resultant quality of coloration depends primarily on the quality of water. Since the hard water is unsuitable, in the case of dyeing the cellulose fibres with reactive dyes, the reproducibility of such a coloring is affected by the minerals coming from hard from water, salt, and the cotton fiber.

The sequestrate agents, representing one of the most significant groups of textile auxiliary agents, are used for softening of water during the dyeing process.

These substances react with the respective metal ions (i.e. Ca^{2+} and Mg^{2+}) without their removal from the system — see Fig. 1.

Traditional chelating agents are polyphosphates, aminopolycarboxylates, hydroxyl-carboxylates, polymeric carboxylic acids, polyaminophosphonates and polyhydroxy-phosphonates [4-6].

Experimental

Used Reactive Dyes

Three reactive dyes of vinylsulphone type were used for dyeing the cotton material; i.e., C.I. Reactive Yellow 5 (Fig. 2), C.I. Reactive Red 198 (Fig. 3), and C.I. reactive Blue 19 (Fig. 4).

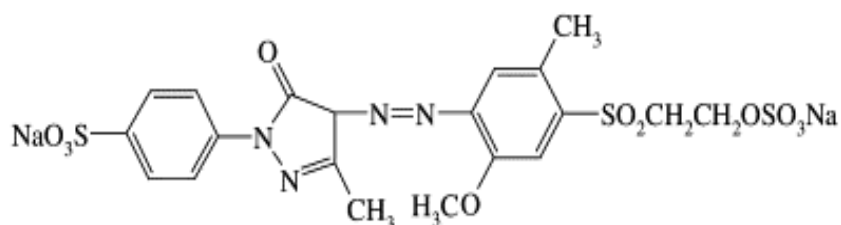


Fig. 2 C.I. Reactive Yellow 15 [7]

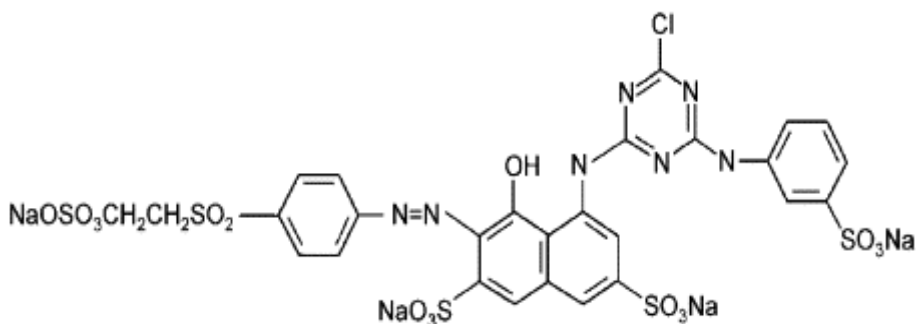


Fig. 3 C.I. Reactive Red 198 [8]

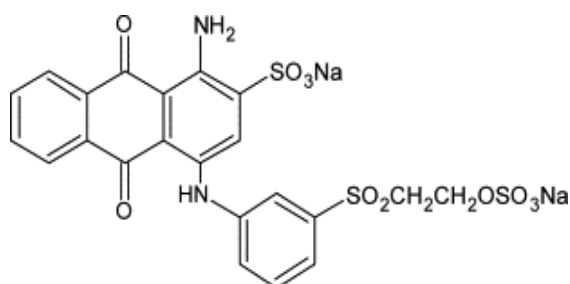


Fig.4 C.I. Reactive Blue 19 [9]

Prepared Sequesterant Agents

Two types of sequesterant agents were prepared; i.e., sample no. 1 (Fig. 5) and sample no. 2 (Fig. 6). In order to compare the efficiency of dyeing, the commercial sequesterant agents Trilon M (Fig. 7) and sequeion 10 Na 430 (Fig. 8) were used.

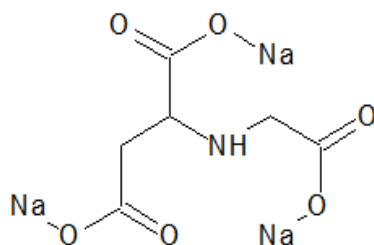


Fig. 5 Sample no. 1

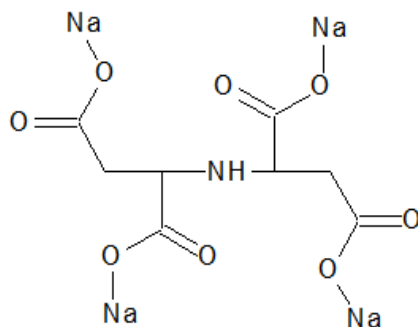


Fig. 6 Sample no.2

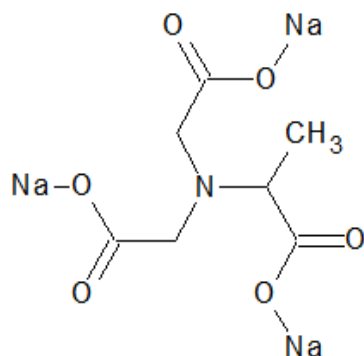


Fig. 7 Trilon M

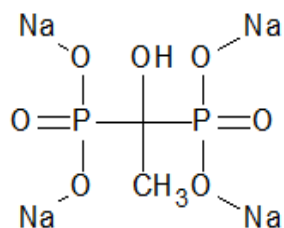


Fig. 8 Sequion 10 Na 430

Dyeing Procedure

In each experiment, the pre-treated cotton fabric (10 g) was used as a material for dyeing; the bath ratio for dyeing being always 1:20. The whole process is depicted in Fig. 9. At the beginning of the dyeing, the bath contained 2 % reactive dye, 1 g l⁻¹ Altaran S8, and 2 g l⁻¹ sequestrate agent (A). After 10 min, 50 g l⁻¹ NaCl was added (B), and subsequently, after further 10 min, 5 g l⁻¹ Na₂CO₃ plus 2 ml l⁻¹ NaOH (38 °Bé) were admixed.

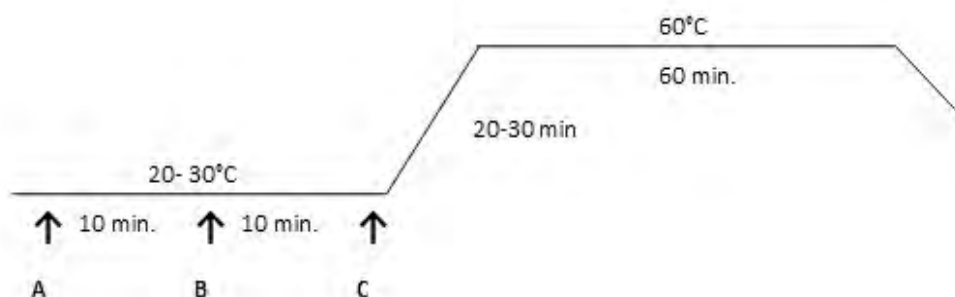


Fig. 9 Process of dyeing

The dyeing was carried out in distilled water and in the prepared hard water of 22° dH in a dyeing machine AHIBA NUANCE TOP SPEED IIB (Datacolor, USA).

The Post-treatment

Such additional treatment is another important part of the dyeing process. Its objective is to remove the unfixed (and hydrolysed) portion of the dye that is incapable to be strongly bound with the substrate. If the washing is not thorough enough, the fastness properties, above all the fastness to perspiration, water, rubbing, and etc., are substantially reduced. After dyeing, the material was thoroughly washed with cold and warm water. This step was followed by a 20-min

soaping under boiling with 1.5 g l^{-1} Syntapon ABA. Finally, the material was rinsed with cold and warm water.

Colour Fastness Test to Washing

First, a combined sample for testing the colour fastness was prepared by clipping the dyed material (B) ($4 \times 10 \text{ cm}$) between the accompanying cotton (C) and wool (D) fabrics, see Fig. 10. All three sheets were sew together (A). The prepared samples were tested in the washing at temperatures of 40, 60, and 95 °C for 30 min. In all cases, the bath ratio was 1:50; the procedure used having corresponded to the ČSN EN ISO 105 c 10 standard.

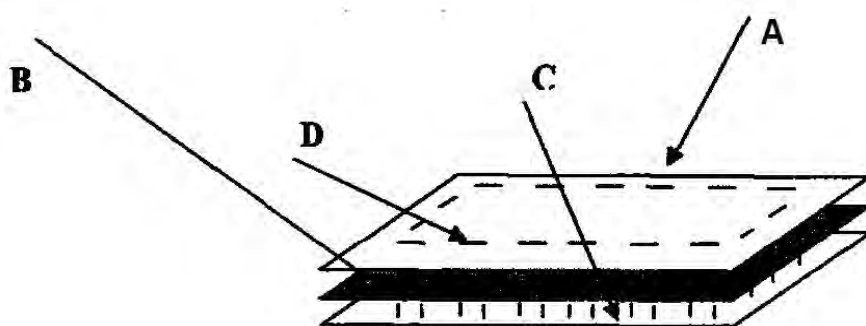


Fig. 10 Combined sample

Measurements

The absorbance before and after dyeing was measured with a spectrophotometer (model SPEKOL 11; Carl Zeiss Jena, Germany). Objective color measurement was then realized by Hunterlab ColorQuest XE (Hunterlab, USA). Measurement of pH, before and after dyeing, was accomplished with a digital pH meter calibrated on a series of commercially available buffers.

Results and Discussion

Tables I-III summarize the experimental values of the degree of exhaustion of the colouring bath used for three dyes examined. The dyeing was started in the distilled water and in hard water without and with the sequestering agents. It has been found that the values of exhaustion of the dye bath for the samples prepared are similar or better as those in Trilon M and Sequion 10 Na 430 and the sample

2 exhibits higher values than sample 1. When using Reactive Yellow 15 and Reactive Blue 19, the degree of exhaustion in hard water with prepared samples was better than that for samples in distilled water.

Table I The value of the degree of exhaustion of dye bath for C.I. Reactive Yellow 15

C.I. Reactive Yellow 15	pH ₁	pH ₂	Absorbance			Exhaustion of dye bath, %
			1	2	3	
Distilled water [DW]	4.08	12.32	0.718	0.257	0.07	64.2
DW + 1	10.70	12.20	0.638	0.317	0.07	50.3
DW + 2	11.38	12.32	0.622	0.266	0.09	57.2
DW + Trilon M	11.70	12.32	0.512	0.284	0.04	44.5
DW + Sequion	11.84	12.27	0.520	0.231	0.05	55.6
Hard water [HW]	4.30	12.35	0.666	0.244	0.08	63.4
HW + 1	10.20	12.25	0.795	0.343	0.07	56.9
HW + 2	9.96	12.04	0.726	0.276	0.10	62.0
HW + Trilon M	11.27	12.30	0.507	0.288	0.05	43.2
HW + Sequion	11.20	12.27	0.692	0.305	0.05	55.9

Table II The value of the degree of exhaustion of dye bath for C.I. Reactive Red 198

C.I. Reactive Red 198	pH ₁	pH ₂	Absorbance			Exhaustion of dye bath, %
			1	2	3	
Distilled water [DW]	4.2	12.3	0.53	0.16	0.1	69.1
DW + 1	10.8	12.2	0.52	0.21	0.1	60.5
DW + 2	11.4	12.3	0.50	0.17	0.1	65.7
DW + Trilon M	11.8	12.4	0.52	0.19	0.1	62.7
DW + Sequion	11.9	12.4	0.52	0.16	0.1	68.8
Hard water [HW]	4.34	12.3	0.58	0.16	0.1	73.1
HW + 1	10.2	12.2	0.52	0.22	0.1	58.1
HW + 2	9.96	12.2	0.54	0.19	0.1	64.6
HW + Trilon M	11.5	12.4	0.52	0.21	0.1	60.6
HW + Sequion	11.5	12.4	0.48	0.27	0.1	44.2

Table III The value of the degree of exhaustion of dye bath for C.I. Reactive Blue 19

C.I. Reactive Blue 19	pH ₁	pH ₂	Absorbance			Exhaustion of dye bath, %
			1	2	3	
Distilled water [DW]	4.09	12.3	0.57	0.1	0.1	87.7
DW + 1	10.9	12.2	0.44	0.14	0.1	67.2
DW + 2	11.5	12.3	0.44	0.1	0.1	78.1
DW + Trilon M	11.8	12.3	0.45	0.12	0.1	74.2
DW + Sequion	11.9	12.3	0.42	0.1	0.1	81.1
Hard water [HW]	4.3	12.3	0.48	0.1	0.1	84.7
HW + 1	10.1	12.3	0.49	0.14	0.1	71.8
HW + 2	9.91	12.3	0.47	0.1	0.1	81.4
HW + Trilon M	11.5	12.4	0.45	0.12	0.1	74.6
HW + Sequion	11.5	12.4	0.45	0.27	0.1	41

Legends: pH₁ – pH value before dyeing, pH₂ – pH value after dyeing; absorbance 1 – value measured in the bath before dyeing, absorbance 2 – measured in the bath after dyeing, absorbance 3 – measured after soaping at the boiling point; HW – hard water, 22° dH

Tables IV-VI describe the change in shade, the difference of shade and the depth of shade. Low differences of shade were reached with the sample 2 that shows good results mainly for C.I. Reactive Blue 19. Sample 1 manifests high values of difference of shade and type depth, too, because this sample probably reacts with reactive dye as it is secondary amine in chemical composition and may therefore react with activated double bond of the reactive dye.

Tables VII-IX survey the data for evaluation of colour fastness test to washing. Reactive dyes are characterized by from good to excellent fastness, which has been validated. Additions of prepared samples to dyeing bath have not negative effect; the highest values of fastness being reached by the C.I. Reactive Red 198.

Table IV Objective colour measurement for C.I. Reactive Yellow 15

C.I. Reactive Yellow 15	ΔE^* against DW	Description	Avg	Wgt
DW + 1	8.84	Lighter, Greener, Less Chromat.	64.84	64.86
DW + 2	3.1	Lighter, Greener, Less Chromat.	86.19	86.27
DW + Trilon M	4.97	Lighter, Greener, Less Chromat.	78.37	78.45
DW + Sequion	0.72	Darker, EQ. Hue, Less Chromat.	97.35	97.41
HW	1.31	Lighter, Redder, Less Chromat.	101.5	102.5
HW + 1	7.19	Lighter, Greener, Less Chromat.	70.5	71.27
HW + 2	2.5	Lighter, Greener, Less Chromat.	89.71	89.74
HW + Trilon M	4.18	Lighter, Greener, Less Chromat.	81.94	82.07
HW + Sequion	0.24	Darker, EQ. Hue, Less Chromat.	100.5	100.5

	ΔE^* against HW			
HW + 1	7.33	Lighter, Greener, Less Chromat.	69.46	69.53
HW + 2	2.67	Lighter, Greener, Less Chromat.	88.39	87.55
HW + Trilon M	4.44	Lighter, Greener, Less Chromat.	80.73	80.07
HW + Sequion	1.07	Lighter, Greener, More Chromat.	99.02	98.04

Table V Objective colour measurement for C.I. Reactive Red 198

C.I. Reactive Red 198	ΔE^* against DW	Description	Avg	Wgt
DW + 1	3.21	Lighter, Bluer, Less Chromat.	80.77	80.89
DW + 2	0.47	Lighter, EQ. Hue, Less Chromat.	96.66	96.72
DW + Trilon M	1.78	Lighter, Bluer, Less Chromat.	88.47	88.56
DW + Sequion	1.16	Darker, Redder, More Chromat.	107.03	106.96
HW	1.29	Darker, Bluer, Less Chromat.	99.84	100.03
HW + 1	3.59	Lighter, Bluer, Less Chromat.	79.93	80.06
HW + 2	0.58	Lighter, EQ. Hue, Less Chromat.	96.01	95.99
HW + Trilon M	1.4	Lighter, Bluer, Less Chromat.	90.74	90.75
HW + Sequion	1.43	Darker, Redder, More Chromat.	109.95	109.86

	ΔE^* against HW			
HW + 1	3.16	Lighter, Bluer, Less Chromat.	80.06	80.04
HW + 2	1.45	Lighter, Redder, More Chromat.	96.16	95.96
HW + Trilon M	1.59	Lighter, Redder, More Chromat.	90.89	90.73
HW + Sequion	2.33	Darker, Redder, More Chromat.	110.13	109.83

Table VI Objective colour measurement for C.I. Reactive Blue 19

C.I. Reactive Blue 19	ΔE^* against DW	Description	Avg	Wgt
DW + 1	6.54	Lighter, Greener, Less Chromat.	66.4	66.55
DW + 2	1.84	Lighter, Greener, Less Chromat.	88.51	88.26
DW + Trilon M	3.59	Lighter, Greener, Less Chromat.	78.43	78.37
DW + Sequion	0.73	Lighter, EQ. Hue, More Chromat.	98.65	98.25
HW	1.56	Lighter, Greener, Less Chromat.	90.2	90.09
HW + 1	7.29	Lighter, Greener, Less Chromat.	62.54	62.62
HW + 2	1.85	Lighter, Greener, Less Chromat.	88.58	88.37
HW + Trilon M	3.71	Lighter, Greener, Less Chromat.	77.6	77.46
HW + Sequion	0.86	Lighter, Greener, Less Chromat.	96.98	96.45
	ΔE^* against HW			
HW + 1	5.77	Lighter, Greener, Less Chromat.	69.34	69.51
HW + 2	0.3	Lighter, EQ. Hue, Less Chromat.	98.21	98.08
HW + Trilon M	2.16	Lighter, Greener, Less Chromat.	86.04	85.98
HW + Sequion	1.3	Darker, Redder, More Chromat.	107.52	107.06

Legends: ΔE^* – difference of shade, Avg – average strength for reflectance, DW – distilled water, Wgt – weighted strength for reflectance, HW – hard water, 22 °dH

Table VII Colour fastness test to washing for C.I. Reactive Yellow 15

C.I. Reactive Yellow 15	40 °C			60 °C			95 °C		
DW	4-5	5	5	4-5	5	4-5	4	5	4-5
DW + 1	4-5	5	5	4	5	5	3-3	5	4-5
DW + 2	4	5	5	4	5	5	3	5	4-5
DW + Trilon M	4	5	5	4	5	5	3	5	4-5
DW + Sequion 10 Na 430	4-5	5	5	4	5	5	3	5	4-5

HW	4-5	5	5	5	5	5	3-4	5	4-5
HW + 1	4-5	5	5	4-5	5	5	3-4	5	4-5
HW + 2	4-5	5	5	4-5	5	5	4	5	4-5
HW + Trilon M	4	5	5	4	5	5	3-4	5	4-5
HW + Sequion 10 Na 430	4-5	5	5	4	5	5	3-4	5	4-5

Table VIII Colour fastness test to washing for C.I. Reactive Red 198

C.I. Reactive Red 198	40 °C			60 °C			95 °C		
DW	4	5	5	4-5	4-5	5	4	4	4-5
DW + 1	4-5	5	5	4-5	5	5	4	4-5	4-5
DW + 2	4-5	5	5	4-5	5	5	4-5	4-5	4-5
DW + Trilon M	4-5	5	5	4-5	5	5	4	4-5	4-5
DW + Sequion 10 Na 430	4-5	5	5	4-5	5	5	4	4-5	4-5

HW	4-5	5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
HW + 1	5	5	5	5	5	5	4	4-5	4-5
HW + 2	4-5	5	5	4-5	5	5	4	4-5	4-5
HW + Trilon M	4-5	5	5	4-5	5	5	4-5	4-5	4-5
HW + Sequion 10 Na 430	4-5	5	5	4-5	5	5	4	4-5	4-5

Table IX Colour fastness test to washing for C.I. Reactive Blue 19

C.I. Reactive Blue 19	40 °C			60 °C			95 °C		
DW	4-5	4-5	5	5	4-5	4-5	3-4	4	2-3
DW + 1	5	5	5	5	4-5	4-5	3	4-5	2-3
DW + 2	5	5	5	5	4-5	4-5	4	4-5	2-3
DW + Trilon M	4-5	5	5	5	4-5	4-5	4	4-5	2-3
DW + Sequion 10 Na 430	5	5	5	5	4-5	4-5	3-4	4	2-3

HW	4-5	5	4-5	4-5	4-5	4-5	4	4-5	2-3
HW + 1	4-5	4-5	4-5	4-5	4-5	4-5	3-4	4-5	2-3
HW + 2	5	4-5	5	5	4-5	4-5	4	4-5	2-3
HW + Trilon M	5	5	5	5	4-5	4-5	3-4	4-5	2-3
HW + Sequion 10 Na 430	4-5	5	5	4-5	4-5	4-5	3-4	4-5	2-3

Conclusion

In this work, possibilities and limitations of the self-sequestering surfactants are outlined with respect to their testing in the model baths for dyeing cotton with vinylsulphon-based reactive dyes. Positive results were reached with sample 2, which had been prepared by reaction of aspartic acid with sodium maleate. In contrast to this, sample 1 was found less effective as it had undesirably reacted with the reactive dye.

The results and observation have indicated that the structure of the dyes used might have an influence on the process of dyeing with the sequestrate agents. This is the case of C.I. Reactive Yellow 15 as the azo dye, of C.I. Reactive Blue 19 as anthraquinone derivative and whereas these two dyes are monofunctional dyes, the C.I. Reactive Red 198 is a heterobifunctional dye. Also, it should be taken into account that, during operational conditions in the industrial use, there is a different situation than that one can keep in a common laboratory – the bath ratio, the respective dyeing material, the concentration of Ca^{2+} making the water hardness, etc. Thus, e.g. the effect of hard water can be more significant compared to the initial expectations.

Last but not least, some results have implied that there is still a lot of experimental material that should be considered in further research.

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