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The Violet Scale, a criterion for assessing the desizing degree of starch-sized fabrics

Report on trials conducted by the working group "Textile Preparation" within the "Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoff-Industrie e.V." (TEGEWA)

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Over 25 years ago, Dr. W. Jülicher [1] published a paper in the trade press dealing with a method to classify enzymatic desizing agents used for starch-sized fabrics. In this article, Dr. Jülicher mentioned possibilities to standardize textile auxiliaries which had been investigated by the working group "Enzyme Products" of the association at that time named "Verband der Textilhilfsmittel-, Lederhilfsmittel- und Gerbstoff-Industrie", the functions of which are now exercised by TEGEWA.

These previous studies had been undertaken in response to demands from the textile industry to develop a method to measure the effect of commercially available starch-degrading enzymes. It had been the objective of these investigations to find a straightforward testing method not involving detailed analyses, i.e. a test that could be made either in a laboratory or even during practical operation.

The method suggested was based on the well-known colour reaction of starch with free iodine: The starch contents of a given fabric (and thus its desizing degree) can be recognized by the colour shade obtained in the iodine test. Unfortunately, the colouration thus achieved was not stable so that it was not possible to keep fabric samples of varying starch contents (and thus differently coloured) for subsequent comparisons. The only manner to preserve the colour shade originally obtained in the test was to take colour photos, a method already suggested by Dr. Jülicher. Yet this was a too complicated method to be carried out in a textile mill, and the shades produced photographically were not found to be absolutely identical with the original.

Therefore, Dr. Jülicher suggested to dye a number of fabric strips in order to obtain a non-fading Violet Scale which could be employed as a comparative yardstick to assess the colour shades achieved in a iodine/starch test and thus to pinpoint the degree of desizing effects obtained.

This scale consisted of 9 fabric strips marked with figures 1 – 9, of which 1 indicated a particularly poor desizing degree, whereas 9 stood for a state of virtually full desizing.

This test method has never been standardized. But the Violet Scale was found an excellent criterion for assessing the effects of enzymes and the degree of desizing obtained in preparation processes and it became generally accepted. The three series issued by the State Examination Office Reutlingen in 1956, 1957 and 1968 are, of course, no longer available, and the office has refused to issue new scales of this type.

The working group "Textile Preparation" within the TEGEWA association therefore decided to compile a completely new series of the Violet Scale.

Unfortunately, the documentation about the production of the first series of the Violet Scale in 1956 is rather poor. Neither was it possible to gather such information from the article of Dr. Jülicher. The only established facts were that "Siriuslicht"-dyestuffs had been used to produce shades 1 to 5, wheras shades 6 to 9 were obtained with Indanthren-dyestuffs. No details of the employed recipe could be ascertained, and there were no indications as to the criteria on which the grades 1 – 9 had been based.

Of course it suggested itself to ask a dyer or a printer to copy the existing scale. This had originally been planned. A new edition was to be produced by printing the respective shades on paper. But there arose the question as to which of the various scales should be copied. Unfortunately, the shades of the old scales were found to greatly differ in some instances.

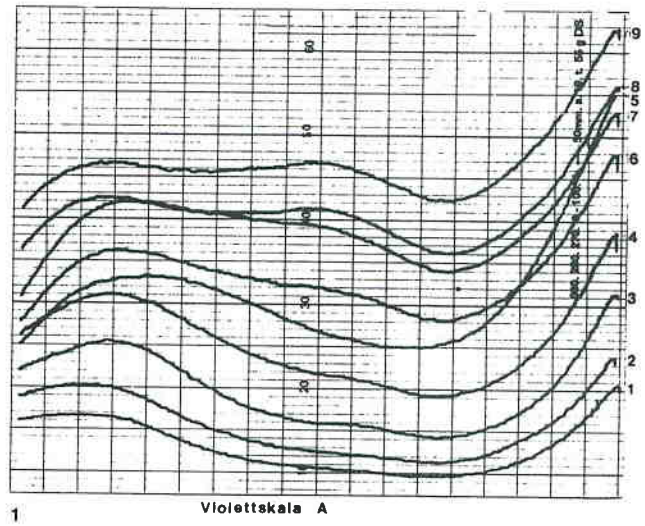
On the other hand, there arose the question whether it could be undertaken to simply copy the shades of the old scale without being aware of the exact criteria that were used when it was originally compiled.

To further investigate this matter, three visually different scales were measured using a recording-type spectrophotometre model DMC (Carl Zeiss) at a measuring distance of 10 nanometres and a range between 380 and 720 nanometres.

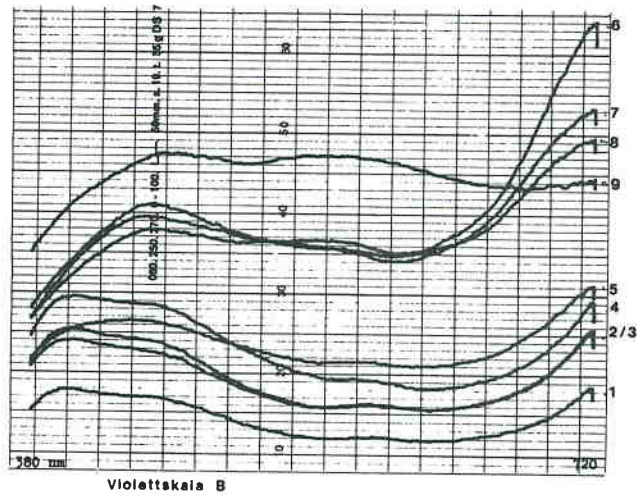
Figs. 1, 2 and 3 show curves thus obtained for Violet Scales A, B and C. The grades 1 – 9 are marked at the right hand side.

From these figures it can be clearly seen that curves A and C show a great similarity whereas scale B differs considerably. Unfortunately, not all scales available could be identified as to their year of issue. It is possible that the three scales used in our experiment originated from three different series. Scale B was found to be definitely of the second issue, whereas scale A can possibly originate from the first or third issue, scale C correspondingly reversed.

On checking scales A and C, it was found that shades 1 and 2 do not differ sufficiently. It is true that this will not make much difference within this range. Shades 7 and 8 coincide within the shorter wave range, shade 5 shows a deviation of colour due to a pronounced deviation within the long wave range. If shade 5 would lie between shades 4 and 6 in this range, the colour graduation could be acceptable. Scale B, however, is completely out of the question.



1 Violettskala A



Violettskala B

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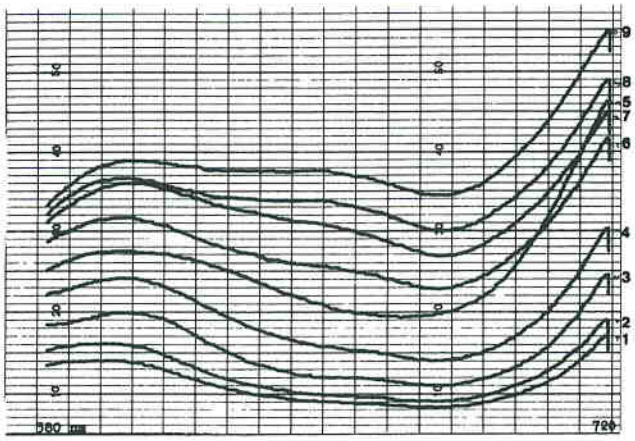

Violettskala C

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Table I Figures applying to Fig. 7

In accordance with data measured by Naujoks/Ney [2]. Material: grey cotton cloth with a starch content of 10.8 on warp threads.

Violet Scale shades	% starch in warp threads	Averaged value	% starch in fabric	% starch logarithmic progression
1	up to 2.5			1.6
2	2.5 – 1.5	2	1	1
3	1.5 – 0.9	1.2	0.6	0.63
4	0.9 – 0.5	0.7	0.35	0.4
5	0.5 – 0.3	0.4	0.2	0.25
6	0.3 – 0.2	0.25	0.125	0.16
7	0.2 – 0.14	0.17	0.085	0.1
8	0.14 – 0.1	0.12	0.06	0.063
9	approx. 0.08	0.08	0.04	0.04

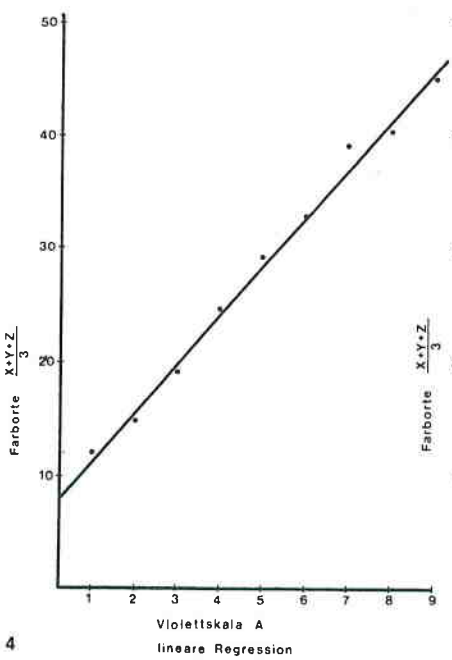
There is another possibility to verify the uniformity of shade graduations by using a graphic representation of the measuring values. For this purpose, measuring values X, Y and Z were averaged and graphically plotted against shades 1 – 9 of the Violet Scale as shown on Figs. 4, 5 and 6 for scales A, B and C.
Using the method of the "linear regression", the averaged measuring values were employed to find the so-called matched straight line, i.e. the straight line having the least distance to all measuring points. In an ideally graduated scale, all measuring points should lie on this straight line. This experiment again proves that scale B is completely out of the question, whereas scales A and C show comparatively low deviations from the straight line, so that the graduation can be regarded as acceptable.
Of course, there remained the interesting question whether the individual graduations of the Violet Scale corresponded with the quantity of residual starch contained in the fabric tested. To clear this question, it was possible to revert to the work of Naujoks/Ney [2]. These authors have taken the trouble to analytically determine the residual starch contents of partly desized fabrics and to compare their findings with the corresponding shade of the Violet Scale. The quantities of starch per warp thread found by these authors have been averaged and converted to values applicable for a fabric. On plotting these starch quantities against the shades of the Violet Scale, a curve as shown on Fig. 7 will be obtained. The only point deviating from the curve line is shade no. 1. Therefore, shades nos 2 and 9 have been employed as corner points in order to obtain a logarithmic progression gradient between these points. The dotted line shows this logarithmic curve. This will make it possible to also find the correct value for shade no. 1 (see Table I).

The striking similarity between the residual starch content found in the analyses of Naujoks/Ney (based on the Violet Scale) and the logarithmic progression will be noted.

Control test:

Bleached cotton fabric (without starch) as well as completely desized unbleached cotton fabric were finished with different add-on quantities of starch. During these finishing processes it was tried to precisely adhere to the logarithmic progression of concentration, beginning with a starch content of 1.6 % (corresponding to shade no. 1) and ending with a starch content of 0.04 % (corresponding to shade no. 9). This involved some difficulties due to the fact that the solutions differed in viscosity and it was not possible to adjust the laboratory padder to an accurate add-on quantity.
A calculation based on the concentrations of the starch solutions and the liquor pick-up values obtained during impregnation resulted in the add-on quantities – in % starch related to the weight of the fabric – shown in Table II.

At the same time, a new Violet Scale was produced, imprinting the respective colour shades on bleached cotton fabric. The pigment printing technique was used.
Fabrics having been finished with differing add-on quantities were then treated with iodine solution, and the colour shades thus obtained were compared with the Violet Scale A as well as with the new Violet Scale (pigment impression).
In this connection, we deem it necessary to comment on the method used for obtaining the violet shades.
Three methods are described in literature:



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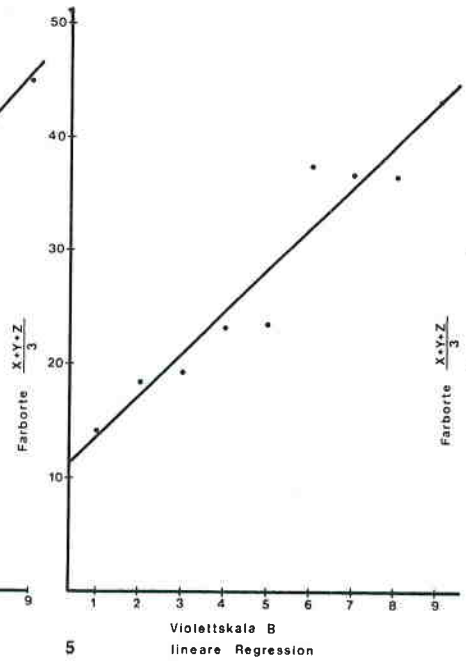

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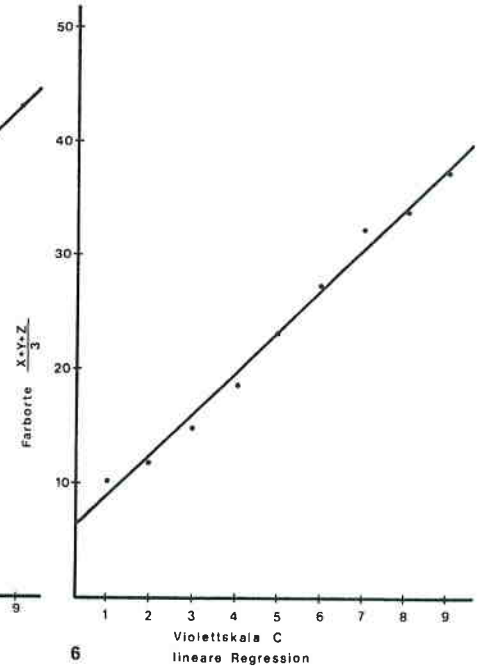

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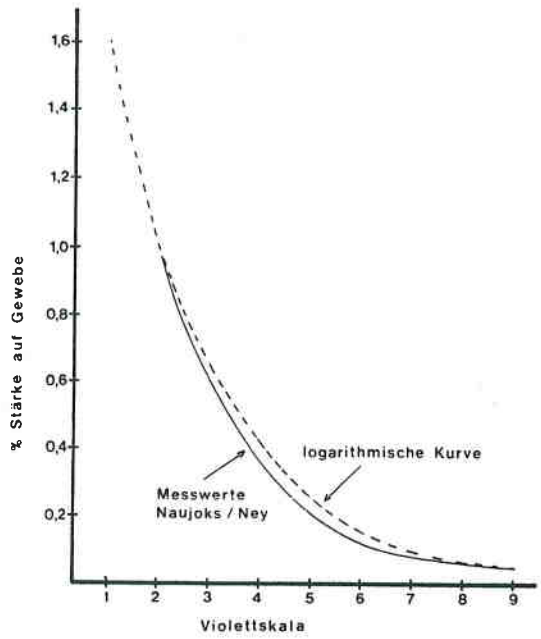
Table II

Sample No.	Ideal value, logarithmic progression	Bleached cotton fabric	Desized cotton fabric
1	1.6	1.63	1.8
2	1.0	0.96	1.0
3	0.63	0.63	0.67
4	0.4	0.39	0.42
5	0.25	0.26	0.25
6	0.16	0.155	0.17
7	0.1	0.096	0.11
8	0.063	0.063	0.07
9	0.04	0.042	0.043



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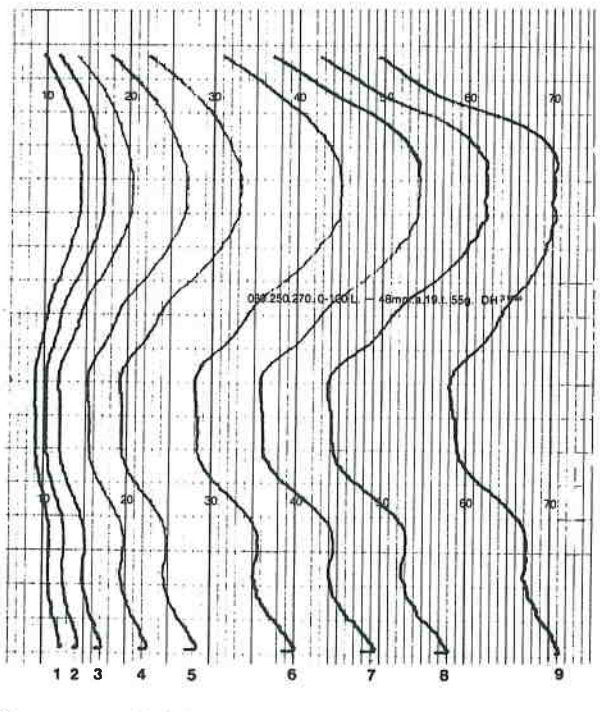


8 Violettskala Pigmentdruck

1. Jülicher [1]:
The sample is placed into a n/200 iodine solution and taken out after a period of 2 minutes. The obtained shade is immediately compared with the scale.

2. Naujoks /Ney [2]:
The sample is inserted into a n/200 iodine solution, taken out after 2 minutes and washed out in water for a short time, followed by superficial drying with filter paper. The sample is then left in the wet state for a period of 5 minutes. Only then, the shade is compared with the Violet Scale.

3. Senner/Badura [3]:
Similar to the method proposed by Naujoks/Ney, however without a specification of time periods to be observed between the test and the comparison with the Violet Scale. The samples were probably compared immediately after the test.

Table III

Unbleached cotton	Accord. to Jülicher Violet Scale		Accord. to Senner/Badura Violet Scale		Accord. to Naujoks/Ney Violet Scale	
	old	new	old	new	old	new
1	1	1	1	1	1	1
2	1	1 – 2	1 – 2	2	2	2 – 3
3	1 – 2	3	3	3	3 – 4	3 – 4
4	3	4	3 – 4	4	5	5
5	4	4 – 5	5 – 6	5	6	6
6	5	5 – 6	6	6	7	7
7	5 – 6	6 – 7	6 – 7	7	9	9
8	7	8	8 – 9	8	9	9
9	8 – 9	9	9	9	9	9
Bleached cotton						
1	1	1	1	1	1	1
2	1	1 – 2	1 – 2	1 – 2	2	2
3	3	3	3	3	3	3
4	3 – 4	4	4	4	5	4 – 5
5	4	5	5 – 6	5	6	6
6	5 – 6	6	6	6	8	7
7	6	7	7	7	9	9
8	7 – 8	8	9	8	9	9
9	9	9	9	9	9	9

It will be noted that there are three different methods of comparison. Therefore, we tested the starch-finished fabrics alternatively with all three methods.
The assessment listed in Table III was made by employees of the Diamalt AG, Munich:

Results of this assessment:

(1) Both Violet Scales are to a large extent similar, but the pigment impression scale yields clearer ratings.

(2) There are no significant differences between the results of trials conducted in accordance with the methods of Jülicher and Senner/Badura. The latter yield slightly better ratings.

(3) The residual starch content values indicated by Naujoks/Ney in relation to the individual colour shades of the Violet Scale could be corroborated in our control test. The test method suggested by these authors results in too "good" ratings in the case of low residual starch content values.

With a view to these results, we came to the conclusion that the graduations of the old Violet Scale could be retained. The new pigment impression of the scale was, however, produced with a view to adhere to the logarithmic progression as far as possible.
Fig. 8 shows the spectrometric curves of the new Violet Scale. Fig. 9 represents the linear regression line of the measured values.
As far as we know iodine solutions of varying concentrations are used for the dyeing tests. Besides the above-mentioned n/200 solution, some mills are reported to use 1/2000 solutions, where 0.5 g of free iodine are contained in a litre. It is recommended to employ the

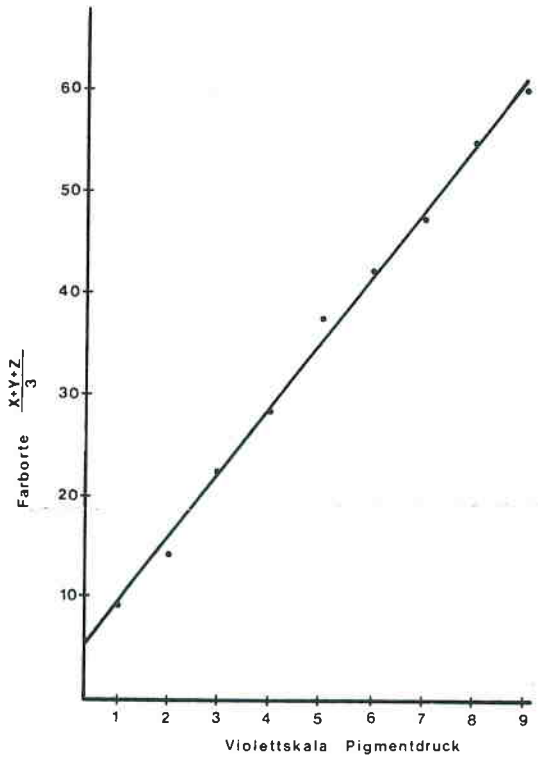
standard solution of n/200 which is frequently mentioned in the literature, although this unit of measurement is no longer valid.

With a view to the above, we recommend the following test procedure:

Immerse a fabric sample in a iodine solution with a concentration of c = 0.005 mol/l for a period of about 1 minute, rinse in water for a short time, dap with filter paper and compare with Violet Scale immediately.

Recipe for the preparation of the iodine solution:

Dissolve 10 g of potassium iodide (KJ) in 100 ml of water, add 0.635 g of iodine, shake or stir until the iodine is completely dissolved. Top up with water to about 800 ml and finally add ethanol to a volume of one litre.
Ethanol is added in order to improve the wettability of the fabric to be tested.



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A more streightforward method of preparation:

Use a commercially available n/100 iodine solution (such as for instance Fixanal or Titrisol) and top up with water and ethyl alcohol to a volume of 2 litres.
On using the Violet Scale it should be borne in mind that it is designed for determination of the desizing degree. A differentiation is only possible for a residual starch content of 1.5 % and lower. Higher starch loadings on the fabric cannot be determined using this method.
A further problem are the shades obtained in the test. Depending on the kind of starch involved and the manner in which it has been disintegrated, varying shades may result which deviate from the Violet Scale to a greater or lesser degree. In this case, it is recommended to assess the depth of the shade. It should furthermore be borne in mind that the practical man will usually follow his usual practice of a quick determination: dripping a few drops of iodine solution on the fabric to be tested and deciding immediately whether the desizing degree is sufficient or not.
It is generally agreed that a desizing degree as per shade no. 6 of the Violet Scale will suffice even for a continuous dyeing operation, provided the desized fabric has good wetting-out properties.
The fabrics for the new Violet Scale were imprinted in the printing laboratory of Hoechst AG with Imperon dyestuffs and were made up by the pattern card department of BASF. The type of the employed fabric and the printing recipes have been deposited with the TEGEWA association to ensure that subsequent reprints can be produced under similar conditions.
The new Violet Scales (Issue October 1981) can be ordered from the TEGEWA association, Karlstrasse 21, D-6000 Frankfurt a. M. 1.

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as well as F. Neugebauer, member of the TEGEWA management.

Literature:

[1] Jülicher, W.: A study of possibilities to standardize testing methods for auxiliaries, Melliand (1956), 1293 – 1294.
[2] Naujoks, E., and P. Ney: The oxydative decomposition of starch sizing finishes with persulphate, Melliand (1976), 401 – 405.
[3] Senner, P., and W. Badura: The oxydative decomposition of starch, RTex 80, vol. 26/27, 78 – 83.

Legends to Figures:

Violettskala = Violet Scale
lineare Regression = linear regression
Meßwerte Naujoks/Ney = measuring values Naujoks/Ney
logarithmische Kurve = logarithmic curve
% Stärke auf Gewebe = % starch on fabric
Violettskala Pigmentdruck = Violet Scale, pigment impression
Farborte = chromaticity