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# The Color of Absorbing Scattering Substrates. I. The Color of Fabrics

E. HOPE ALLEN* and G. GOLDFINGER, *North Carolina State University at Raleigh School of Textiles, Raleigh, North Carolina* 27607

## Synopsis

A treatment of the color of textile materials is proposed which is an extension of G. G. Stokes' "pile of plates" problem. Unlike the conventional treatment of this subject, e.g., that by Kubelka and Munk, this approach permits independent determination of all variables: coefficient of absorption of the dye, refractive indexes of the fibers, the effect on color of the geometry of the fabric and yarn, and the distribution of the dye within the fiber. Here, cylindrical, optically homogeneous fibers in a parallel array are assumed. Experimental data show that this treatment predicts far more satisfactorily the color of fabrics at high dye concentrations and low reflectance values than does the Kubelka-Munk approach.

## INTRODUCTION

Kubelka and Munk[1,2] described the color of absorbing-scattering substrates in terms of a quantity $K/S$, where $K$ is the coefficient of absorption, and $S$, the one of scattering, and where, under a wide variety of reflectance conditions, the ratio can be taken to be proportional to the concentration of the colorant. Among several treatments of the problem of relating colorant concentration to reflected color,[3] this one has enjoyed widest acceptance in the textile industry.

Within the limitation of the Kubelka-Munk treatment, it should be possible to predict the color of a textile material viewed in a medium of one refractive index, air, from its color when viewed in another, for example, water ($n_D = 1.33$). (The practical importance of this is obvious and need not be discussed here.) Experimental evidence[4] indicates that the limitations of the Kubelka-Munk treatment are too restrictive to leave room for any worthwhile predictions of this nature.

The work, the first step of which is reported here, has been undertaken because of the need for a "better" theory. Also, the Kubelka-Munk approach is esthetically not satisfying: (a) $K$ and $S$ cannot be determined by independent measurements; (b) the absorbing-scattering substrate has to be treated as a continuum which a textile material, in most cases, manifestly is not (e.g., for all practical purposes, the diameter of textile single fibers is between 10 and 100 $\mu$).

* Present address: Lehigh University, Bethlehem, Pennsylvania.

Beginning with Stokes[5] in 1860, several authors,[6–9,12] including Kubelka,[13] have treated the problem of reflectance by and transmittance through "a pile of parallel plates." One can, of course, consider each "plate" as an array of fibers, that is to say, one sheet of a fabric. Such an approach meets one of the objections to the Kubelka-Munk treatment.

The approach outlined here is based on the "pile of plates" model. However, unlike the Kubelka treatment, it leaves open the possibility to consider the geometry of the array constituting the plate. It also permits one to include the effect of the coefficient of absorption of the fiber–dye system, the refractive indexes of the fiber, and the distribution of the dye in the fiber on the color of the textile substrate. Conceptually, this treatment is a special case of those which preceded it; but mathematically, it reduces to the cases referred to above.

In this first treatment, we assume that each "plate" consists of a parallel array of isotropic cylinders of equal diameters which are large compared to the wavelength of light. In these cylinders the dye is uniformly distributed. The "plates" are immersed in an optically transparent, continuous medium.

The two variables used are $CK$, the product of the coefficient of absorption (per radius of the fiber) of the dye times its concentration, and $m$, the ratio of the refractive index of the fiber, $n_2$, to that of the continuous medium, $n_1$.

## MATHEMATICAL TREATMENT

### Model of the Fabric

It is assumed that the absorbing–scattering substrate consists of a number of distinct layers of infinitely wide arrays of isotropic cylindrical fibers (Fig. 1a), such that light of intensity $i_0 = 1$, incident on an array,

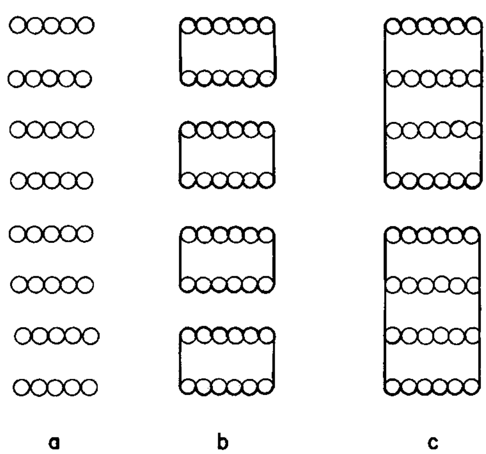


Fig. 1. (a) Cross section through model of fabric; (b) representation of grouping of absorbing–scattering arrays for the first iteration; (c) representation of grouping of absorbing–scattering arrays for the second iteration.

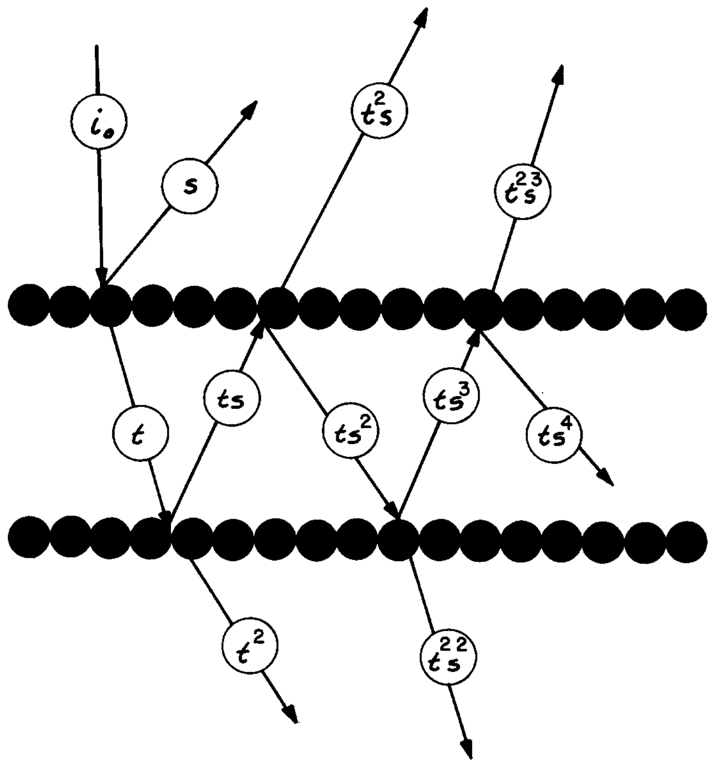


Fig. 2. The reflection and refraction patterns on the first two layers of fabrics.

causes one of three things to occur (Fig. 2): (a) it is reflected or refracted back in the general direction opposite to that of the light incident on it; (b) it is reflected or refracted in the same direction as the light incident on it; and (c) finally, it is neither reflected nor refracted, in which case it is absorbed (fluorescence is not now considered). It follows, therefore, that

$$s + t + a = i_0\, dd = 1 \tag{1}$$

where $s$ is the energy reflected or refracted in the direction opposite to that of $i_0\, dd$, $t$ is the energy reflected or refracted in the direction of $i_0\, dd$, and $a$ is the energy absorbed.

We can consider the events taking place on the first pair of arrays (Fig. 1a) as follows: the incident light, a parallel monochromatic bundle, strikes the first layer and may be reflected from the surface of the constituent fibers or refracted by them in a manner such that its vector projection onto a coordinate normal to the enveloping boundary has a sign opposite to that associated with the incident beam (Fig. 2). The light may also be reflected or refracted in a manner such that an analogous treatment leads to a vector projection of opposite sign.

By eq. (1), the light not accounted for, which is, of course, the absorbed portion $a$, is given by

$$1 - a = s + t \tag{2}$$

and, setting $t = ks$,

$$s = \frac{1 - a}{1 + k} \tag{3}$$

and

$$t = k\left(\frac{1 - a}{1 + k}\right) \tag{4}$$

Since $i_0\, dd$ was set to equal 1, $t$ represents the fraction of the energy incident on the second layer; and from that $t^2$ is the fraction transmitted through both layers in this first sequence of events, assuming that the angular distribution of the radiation remains the same for each layer. However, the light back reflected from the second layer might also be reversed in direction a second time on the first layer, and thus one arrives at the total light energy transmitted through the first pair of layers:

$$\tau_1 = \frac{t^2}{1 - s^2} = \frac{k^2(1 - a)^2}{(1 + k)^2 - (1 - a)^2} \tag{5}$$

Through similar consideration, we can calculate the fraction of the incident energy reflected by this set of two arrays of fibers:

$$\sigma_1 = s\left(1 + \frac{t^2}{1 - s^2}\right) = s(1 + \tau_1) = \frac{1 - a}{1 + k}(1 + \tau_1) \tag{6}$$

This entire argument can now be repeated by considering the first two layers as forming a new single array and, similarly, the third and fourth layers constituting a second array (Fig. 1b). Thus, in general terms,

$$\sigma_n = \sigma_{n-1}(1 + \tau_n) \tag{7}$$

and

$$\tau_n = \frac{\tau^2_{n-1}}{1 - \sigma^2_{n-1}} \tag{8}$$

After establishing the values of $a$ and $k$, the function $\sigma$ can be evaluated numerically.

## The Value of $a$

By the laws of optics,

$$m \sin \alpha = \sin \theta \tag{9}$$

where $\theta$ is the angle of incidence and $\alpha$ is that of refraction; $m = n_2/n_1$, as defined above. If we set the radius of the circle representing a cross

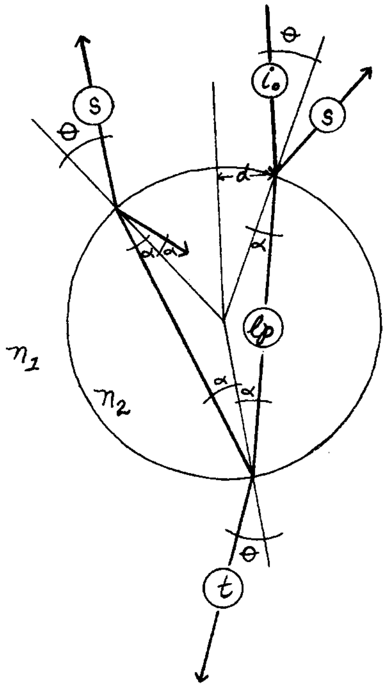


Fig. 3. Cross section through fiber and the path of reflected and refracted light. Determination of $a$.

section of a cylindrical fiber equal to 1 (Fig. 3), then $\sin \theta = d$, and $\sin \alpha = \dfrac{d}{m}$.

The length of the path traveled by refracted light $lp$ is

$$lp = 2 \cos \alpha = 2 \sqrt{1 - \frac{d^2}{m^2}} \tag{10}$$

for each step of the refraction.

The fraction of light transmitted through the fiber between the point of internal refraction and first internal reflection is

$$e = 10^{-CK2\sqrt{1-d^2/m^2}} \tag{11}$$

where $CK$ is the product of the coefficient of absorption per unit radius and the concentration of colorant.

The light energy initially refracted is $i_0\, dd(1 - \rho)$, where $\rho$ is given by the appropriate form of the Fresnel equations. Thus, setting again $i_0 = 1$, and writing $e$ for $10^{-CK2\sqrt{1-d^2/m^2}}$ on the first path, $(1 - \rho)e$ of the light is transmitted, and $(1 - \rho) - (1 - \rho)e = (1 - \rho)(1 - e)$ is absorbed. Through the second path the transmitted amount is $(1 - \rho)e\rho$, and, of course, $(1 - \rho)e\rho - (1 - \rho)e^2\rho = (1 - \rho)e\rho(1 - e)$ is absorbed. Summing over an infinite number of steps, one obtains

$$a = (1 - \rho)\cdot(1 - e)/(1 - e\rho) \tag{12}$$

where $\rho$ has two values, which have to be handled separately for the parallel and perpendicular polarization components of the radiation:

$$\rho_{\|} = \left(\frac{\cos\theta - \sqrt{m^2 - \sin^2\theta}}{\cos\theta + \sqrt{m^2 - \sin^2\theta}}\right)^2 = \left(\frac{\sqrt{1 - d^2} - \sqrt{m^2 - d^2}}{\sqrt{1 - d^2} + \sqrt{m^2 - d^2}}\right)^2 \tag{13}$$

and

$$\rho_{\perp} = \left(\frac{m^2\cos\theta - \sqrt{m^2 - \sin^2\theta}}{m^2\cos\theta + \sqrt{m^2 - \sin^2\theta}}\right)^2 = \left(\frac{m^2\sqrt{1 - d^2} - \sqrt{m^2 - d^2}}{m^2\sqrt{1 - d^2} + \sqrt{m^2 - d^2}}\right)^2. \tag{14}$$

Thus, throughout the calculation, eq. (12) will be handled separately for $\rho = \rho_{\|}$ and $\rho = \rho_{\perp}$, and numerical integration will be carried out for the values of $a$ calculated from $d = 0$ to $d = 1$.

## Calculation of $k$

The $k = t/s$ value gives the ratio of the energy reflected and refracted downward to that reflected and refracted upward across the plane defining the surface of the sample. The value of $k$ is a function both of $m$, the refractive index ratio, and $a$, the absorption. Under the limiting condition that all refracted light is absorbed by the fiber, $k$ is entirely dominated by reflection. As can easily be seen, for values of $d = 0$ to $d = 0.707$ ($\theta = 0°$ to $\theta = 45°$) the reflection is upward in Figure 4, and for values of $d = 0.707$ to $d = 1$ ($\theta = 45°$ to $\theta = 90°$), downward.

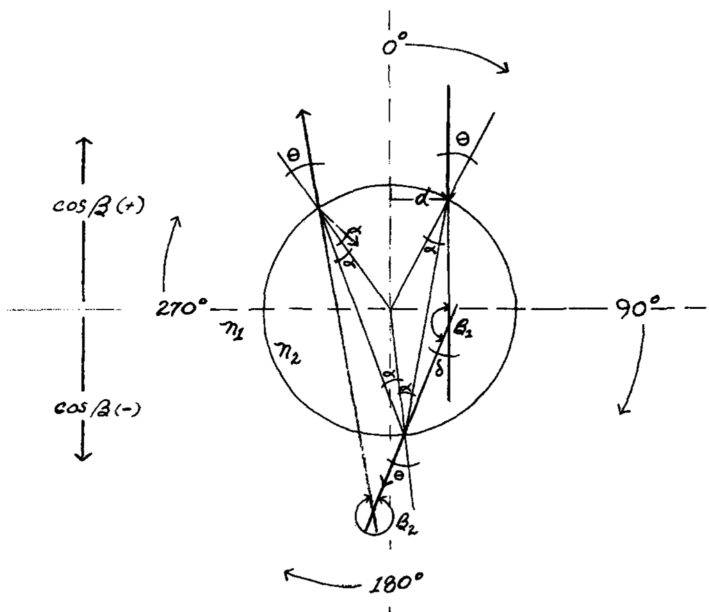


**Fig. 4. Determination of the direction of refraction for the calculation of $k$.**

To calculate the direction of the refracted radiation an auxiliary quantity, the angle $\beta$ is used.

Figure 4 shows that if $\beta$ is between 270° and 90°, in the upper half (in other words, if cos $\beta$ is positive), the first refraction is upward; and if $\beta$ is between 90° and −270°, in the lower half (if cos $\beta$ is negative), the first refraction is downward. (From Fig. 4 it can be seen that $\beta_1 = 180° - 2(\theta - \alpha)$.)

This can be transcribed in the now familiar terms of $d$ and $m$ as

$$\cos \beta_1 = -\left\{[2(1 - d^2) - 1]\left[2\left(1 \mp \frac{d^2}{m^2}\right) - 1\right] + 2d\sqrt{1 - d^2}\left(2d/m\sqrt{1 - \frac{d^2}{m^2}}\right)\right\}$$

or

$$\cos \beta_1 = -(1 - 2d^2)\left(1 - 2\frac{d^2}{m^2}\right) - 4\frac{d^2}{m^2}\sqrt{1 - d^2}\sqrt{1 - \frac{d^2}{m^2}} \quad (15)$$

For the second refraction, $\beta_2 = \beta_1 + (180 - 2\alpha)$. Subsequent refractions, $n = 1,2,3\ldots$, increase the angle $\beta_n$ by this same value, $(180 - 2\alpha)$. In our now familiar form of expression,

$$\cos \beta_n = \cos \beta_{n-1}\left(2\frac{d^2}{m^2} - 1\right) - \sin \beta_{n-1}\left(2\frac{d^2}{m^2}\sqrt{1 - \frac{d^2}{m^2}}\right) \quad (16)$$

The value of $k$ can be summarized as

$$k = \frac{t}{s} = \frac{\rho_{d=.707\to 1.0} + (1 - \rho)^2(e_{\cos\beta_1(-)} + \cdots + e^n\rho^{n-1}{}_{\cos\beta n(-)})}{\rho_{d=0\to .707} + (1 - \rho)^2(e_{\cos\beta_1(+)} + \ldots + e^n\rho^{n-1}{}_{\cos\beta n(+)})}$$

weighted for parallel and perpendicular polarized portions of the radiation (with the appropriate values substituted for the $\rho$'s) and the numerical summation carried out separately according to the constraints indicated in the subscripts.

## LIMITING ASSUMPTIONS

The limiting assumptions made to simplify the problem fall into two categories: (1) geometric assumptions, (2) optical simplifications.

**Geometric Assumptions.** As mentioned before, the model assumes for each layer an array of cylindrical fibers of finite thickness which does, in fact, conform with physical reality. It also assumes that these fibers are so closely packed that *all* incident light interacts with fibers in each array. Simultaneously, however, the contradictory assumption is made that fibers within each array do not interact with the optical pattern of reflection–refraction for adjacent fibers. It is hoped that this contradiction will prove tolerable, since estimating the effects of interaction is no less difficult than correcting for them. (An exact treatment of this problem of fabric geometry is at present under way.)

The assumption that the fibers are cylinders of equal diameter is often also untrue, and, in practice, arrays of fibers are far more complex than assumed here. This is a problem with which we plan to deal later.

**Optical Assumptions.** The assumption of optical isotropy is manifestly untrue for fibers. It is hoped that the *average* index of refraction is an adequate approximation.

The diameter of the fibers, which in practice is at least 20 times the wavelength of light in question, is adequate justification for the naive geometry of the reflection–refraction model. It is hoped that this simple reflection–refraction pattern is adequate and that any fine structure of reflection refraction resulting from interference cancels adequately.

No provision is made for the indefinite value of the index of refraction at absorption peaks in the hope that this effect is effectively averaged.

## RESULTS

A computer program has been written to calculate $\sigma$ for values of $m = n_2$ (fiber)$/n_1$ (medium) $= 1.0, 1.1, \ldots 2.0$ and $CK = 0$ (for entirely transparent fibers) to $CK = 8.5$ (for which $\sigma$ is less than 0.01). (Because the number 8.5 appears in a double exponential it is the largest value that could be handled in a Fortran IV program.) The numerical summation of the $\sigma$ values was extended to $\tau_n < 10^{-6}\ \sigma_n$.

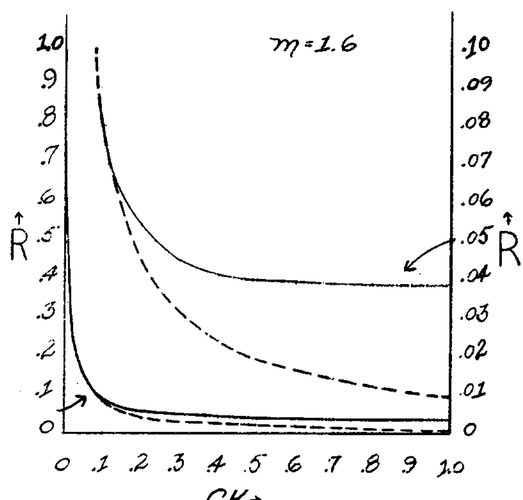


Fig. 5. Continuous line is a plot of the reflectance $R$ vs. the product of the dye concentration and its coefficient of absorption $CK$ for a refractive index ratio $m = 1.6$ calculated from this treatment. Dotted line is the corresponding Kubelka-Munk curve. A coefficient $f = 49.5$ for the relationship $f \cdot CK = K/S$ has been determined from the points for $CK$ from 0 to 0.1. ($R$, the symbol customary in textile technology, is used instead of $\sigma_n$.)

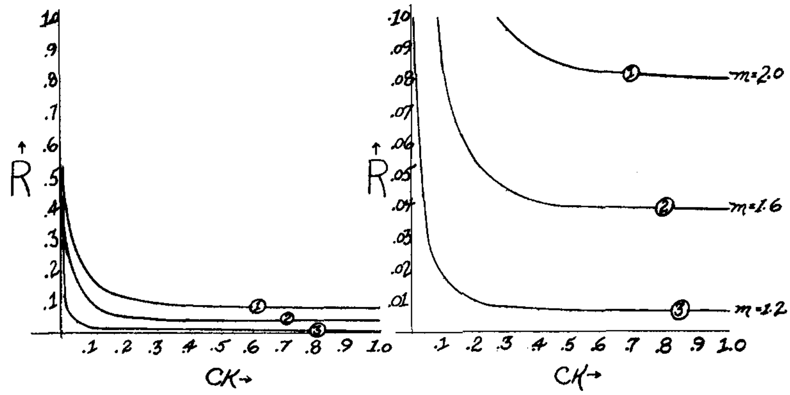


Fig. 6. Reflectances $R$ for various values of $m$, the refractive index ratio, are plotted vs. $CK$. ($R$, the symbol customary in textile technology, is used instead of $\sigma_n$.)

It has been shown in previous papers[4,11] that the plot of the ratio of reflectance values obtained for dry and wet samples against the reflectance of the dry samples indicates that the Kubelka-Munk treatment is inadequate to predict the results. Figure 5 compares the Kubelka-Munk prediction to one based on this approach for $m = 1.6$. For $CK$ values below 0.1, the two curves coincide if the relationship $K/S = 49.5CK$ is assumed. However, at higher values of absorbance, lower values of reflectance, our treatment predicts higher reflectance values than those by Kubelka and Munk. It is, of course, well known that for high dye concentrations the Kubelka-Munk equation has to be corrected in the direction of higher reflectance to provide proper predictions.

In Figure 6, $R$ versus $CK$ is shown for several values of $m$, the refractive index ratio.

## CONCLUSIONS

The Kubelka-Munk theory of the color of absorbing–scattering substrates has been formulated for paint films, in which colored (absorbing) and white (scattering) particles are distributed in a vehicle (e.g., drying oil), which constitutes the continuous medium. The very wide applicability of this treatment amply proves the soundness of its limiting assumptions. In the case of textiles, the theory is notoriously undependable at high dye concentrations or low reflectance values. This can in practice be taken care of by correcting terms.

The approach here suggested has advantages over the theory of Kubelka and Munk:

1. It contains the means of refinement to account for conditions encountered with textiles, such as nonuniformity of dye distribution, surface effects of the fibers, absorbing–scattering events within the fibers, etc.

2. It conforms in its discontinuous model more closely to the physical reality with all its attendant objective and subjective advantages.

3. It is based on independently measurable quantities; refractive indexes, absorption coefficients of the dyed fibers, and cross-sectional dimensions (in the simplest case, fiber radius).

4. It permits (in its more refined form) calculation of the effect on the color of the textile material of nonuniform dye distribution, cross-sectional dimensions, shapes and surface characteristics of fibers, and fabric and yarn geometries. This permits optimizing technical, economic, and marketing considerations.

Work along those lines is in progress, in part completed, and will be published as experimental verification becomes available.

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## References

1. P. Kubelka and F. Munk, *Z. Tech. Phys.*, **12**, 593 (1931).
2. P. Kubelka, *J. Opt. Soc. Amer.*, **38**, 448 (1948).
3. J. L. Saunderson, *J. Opt. Soc. Amer.*, **32**, 727 (1942).
4. E. H. Allen et al., *J. Polym. Sci.*, **B10**, 203 (1972).
5. G. G. Stokes, *Proc. Roy. Soc.* (London), **11**, 545 (1860–62).
6. T. H. Gronwall, *Phys. Rev.*, **27**, 277 (1926).
7. F. Benford, *J. Opt. Soc. Amer.*, **36**, 524 (1946).
8. P. D. Johnson, *J. Opt. Soc. Amer.*, **42**, 978 (1952).
9. N. T. Melamed, *J. Appl. Phys.*, **34**, 560 (1963).
10. P. Kubelka, *J. Opt. Soc. Amer.*, **44**, 330 (1954).
11. G. Goldfinger, H. S. Goldfinger, S. P. Hersh, and T. M. Leonard, *J. Polym. Sci.*, **C31**, 25 (1970); E. Hope Allen and G. Goldfinger, *Text. Chem. Color.*, **3**, 289/53 (1971).
12. A. M. Scallan and J. Borch, *Tappi*, **55**, 583 (1972).

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