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The brighter white appears clean and beautiful and human eye loves it. Man's efforts to obtain a pure white probably started from very early times. Perhaps the pure white of snow or clouds in the azure sky might have inspired the man to search agents causing whiteness to the yellowed man-made so-called white articles.

For this purpose various procedures are tried, among them, one is chemical bleaching. By chemical bleaching, the coloured impurities are either destroyed or decolorised. For decolourization, either oxidation or reduction reactions are used and this procedure was followed by Physical Bleaching.

It had been known that yellowish material could be made to look considerably whiter by light tinting with blue dyes. In this process known as tinting - a small portion of a complementary colour blue is superimposed on the pale yellow light reflected by the substrate. Due to this, reduction occurs slightly in the total light reflected from the substrate so that material appears dull i.e. less brilliant.

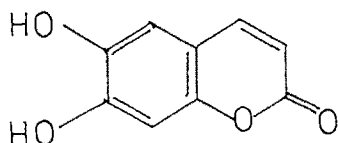
This couldn't satisfy the textile world. However, Nature provided the Scientists and Researchers the way to success.

The theoretical basis for such research was provided by the physicist George Gabriel Stokes in 1852 when he described the phenomenon of FLUORESCENCE. Fluorite and uranium glass which are capable of converting invisible

ultraviolet rays into visible light were described as examples.

V. Lagorio established in 1921 in his paper - "Colorimetry and the significance of fluorescence and polarization for measurements" that, fluorescent dyeing apparently reflects more visible light than the amount incident on them. This prepared the way for the development of fluorescent whitening agents.

The first step in this direction was taken in 1929 when Paul Kraus who tried horse-chestnut husk extract<sup>1</sup> for whitening purpose. He soaked semi-bleached flax yarn in horse-chestnut husk extract and made the whitest white known at that time even whiter. The active ingredient in this process was aesculin, a blue fluorescent glucoside of 6,7-dihydroxy coumarin (1)



( 1 )

However, this compound developed discolouration on exposure of the fabric to light so rapidly, that the discovery remained hidden.

The aesculin was absorbing the ultraviolet portion of daylight and emitting this as a blue light, so that the pale yellow hue of the fabric appeared whiter and as a result of the increase in the reflected light, it appeared more brilliant also.

E. Allen<sup>2</sup> and R.S. Hunter<sup>3</sup> and others have conducted and reported work which resulted in practical ways and means of defining and measuring whiteness.<sup>4</sup>

It is characteristic of optical brighteners that, they absorb invisible light in the uv region of the spectrum and transform it into visible light in the blue region. Both absorption and fluorescence can be measured spectrophotometrically. Ideal uv absorber absorbs the entire long wave uv component from daylight. It emits no radiant energy.<sup>5</sup>

All fluorescent brighteners emit predominantly in the blue region as human eye associates blueness with the white. However, the colour association with white is evaluated in different ways. Although in Europe, preference is given to a blue to violet white, in the United States, a white with a greenish blue tint is more appreciated.<sup>4</sup>

Prior to the discovery of the fluorescent brighteners, the whiteness was defined as the total of reflected light relative to the ideal reflection of MgO standard. The percentage of whiteness can be exceeded above 100 % reflectance of the magnesium oxide by adding the blue light to substrate.<sup>4</sup>

So, today the ideal white not only reflects all incident light but adds blue reflectance.<sup>4</sup>

In the raw or undyed state articles such as textiles, paper and plastics which are composed mainly of organic materials, absorb some of the daylight which strikes them

particularly in the blue range of 400 - 480 nm range. This results in the yellowish hue of the material giving it an yellowish dull appearance [Fig 1 (a)].

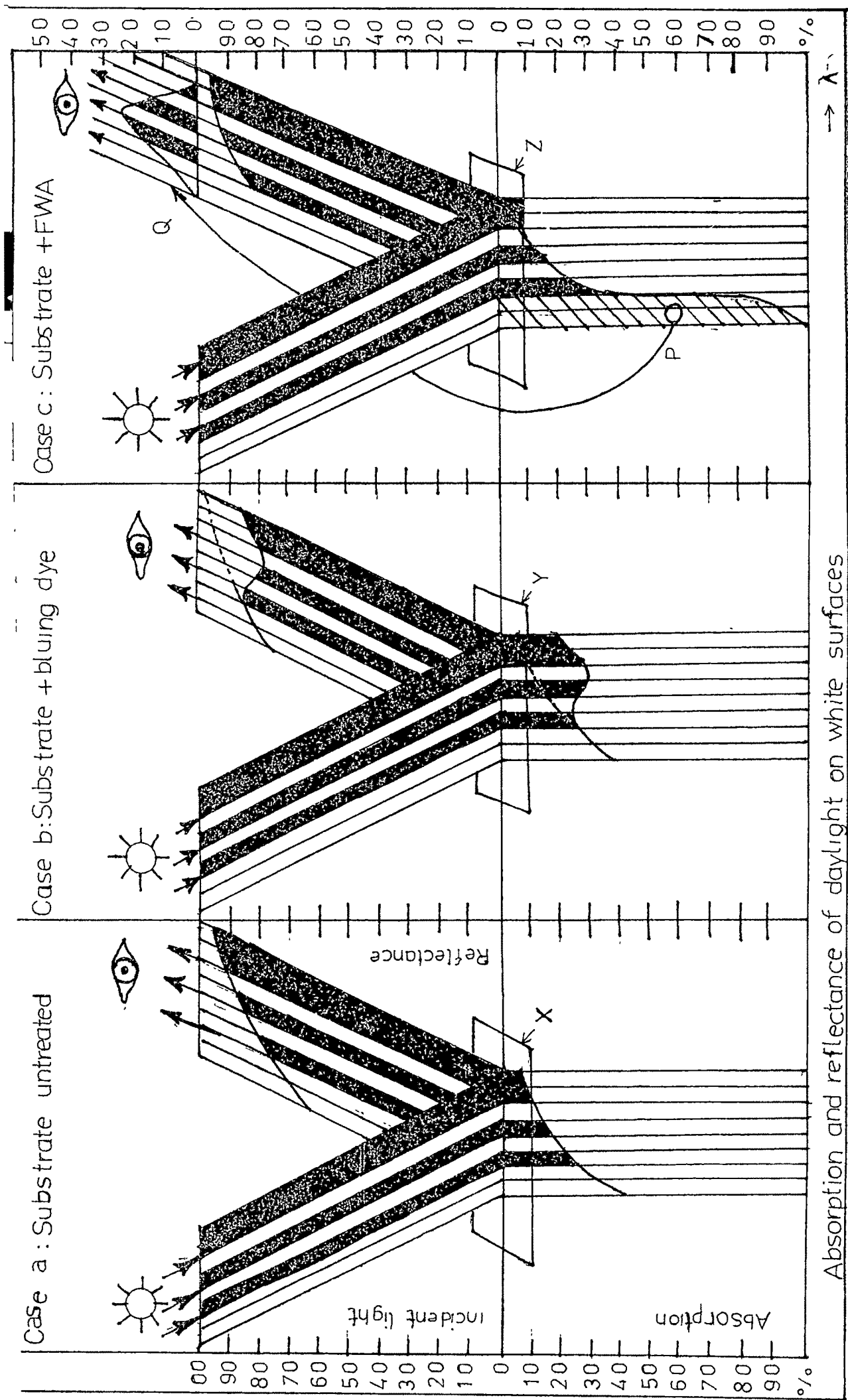
This yellow tint which is generally described as a "blue defect" is attributable to coloured impurities which can be reduced by chemical bleaching.

The blue defect can also be corrected by addition of a blue dye to the material. This causes compensation for dull yellow appearance, because, the blue dye absorbs the excess yellow portion of the light to produce a relative increase in the complementary blue portion in the reflected light. This makes the object appear whiter. The correction is only obtained at the expense of light reflected and hence the object appears still dull due to decrease in the reflected light which cannot satisfy the requirement of white completely and satisfactorily [Fig 1 (b)].

The application of the fluorescent brightening agent not only can correct the blue defect but also offer to the material extra brilliance, extra whiteness and extra brightness<sup>1</sup> [Fig.1(c)].

The mechanism can be explained in terms of quantum theory of light and electronic structure of atoms and molecules.<sup>6</sup>

When light falls on organic substance in solution or on a substrate, some light is absorbed and rest is reflected. The light quanta absorbed are normally dissipated <sup>at</sup> in the form of the <sub>λ</sub>



Absorption and reflectance of daylight on white surfaces

- X = Substrate - yellowish white .
- Y = Substrate - whiter, but less bright .
- Z = Substrate - whiter, brighter, brilliant .

P = Absorbed UV light

Q = Emitted fluorescent light

CT

heat energy.<sup>5</sup>

Fluorescent whiteners are able to provide the blue violet light needed to compensate the yellow without themselves absorbing any visible light. The daylight contains considerable ultraviolet component in the 300-400 nm range. While not absorbing any light in the visible portion the whitener absorbs the uv - component which is not visible to human eye and emits the energy absorbed in the form of visible light in the longer wavelength region (400 - 500 nm).

As a result of this light conversion, the object apparently reflects more visible light than was originally incident on it and therefore appears not only whiter but also brilliant and brighter.<sup>5</sup>

The physical conception of the process of fluorescence is based on the energy present in the molecules or atomic groups in the ground state and in excited state. [Atomic vibrations and the electron transitions during the absorption of energy, which can be described with the aid of R.W.Pohl's mechanical model and the Franck-Condon principle.] An electron transition occurs in a shorter time than the vibration period of the atom and therefore does not change the atom's kinetic energy. The distance between the atomic nuclei remains unchanged.

NO  
verb  
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By absorbing energy photons from uv light, the internal energy of the whitener molecule is raised from the ground state,  $S_0$  into a higher excited electronic state  $S_1$  or  $S_2$  (excited

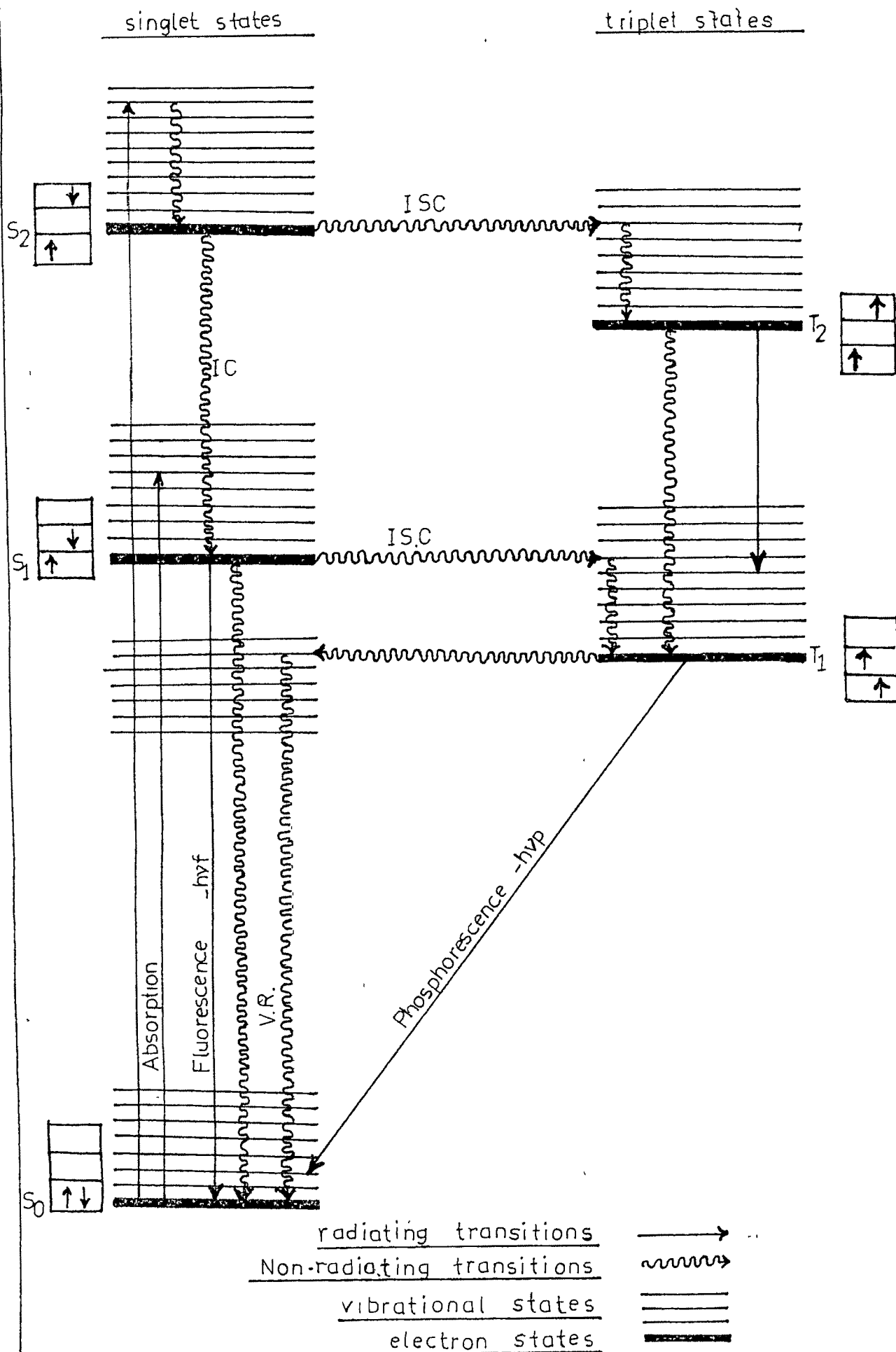
singlet states) for example, as a result of non-radiating deactivation (vibrational relaxation) within  $10^{-13}$  sec., the molecule returns to the lowest level of the excited singlet state ( $S_2$ ). With further non-radiating energy loss the molecule enters the singlet ( $S_1$ ) state, after approximately  $10^{-11}$  secs and remains in this state for some  $10^{-8}$  sec.<sup>5</sup> This is called internal conversion or IC [Fig.(2)].

It then returns to the ground state. This final transition being accompanied by light emission-fluorescence [Fig.(2)].

Since energy was lost without any radiation in the earlier phases, the photons emitted have less energy i.e. the light is of larger wavelength. According to Stokes's law - a good whitener should have a quantum yield of 1 i.e. one light quantum should be emitted for each light quantum absorbed.

But the quantum yield of 1 is only rarely obtained. This can be attributed to various processes of non-radiating deactivation of the electronically excited states, such as intercombination transitions<sup>5</sup> or Intersystem crossing into triplet states which compete as it were with fluorescence. The phenomenon is referred to fluorescence quenching. Even a small amount of foreign matter or impurities may totally or partially quench fluorescence by taking away the exciting energy from the fluorescent compound.<sup>5</sup>

The average mean life of the excited molecule is  $10^{-8}$  to  $10^{-9}$  sec and shorter this life the less will be the





the difference in wavelengths of emitted and absorbed lights and greater will be the fluorescence as there will be lesser time for dissipation of energy as heat.<sup>6</sup> Though industrial development in this field began in 1935, In 1934, ICI had pointed out that, dyed bleached cotton textiles which were treated with bisbenzoyl derivatives of 4,4' diamino stilbene 2,2' disulfonic acid - produced fluorescence when irradiated with uv light. The fluorescent brightener of following constitution was marketed as 'Solium' after the world war II.

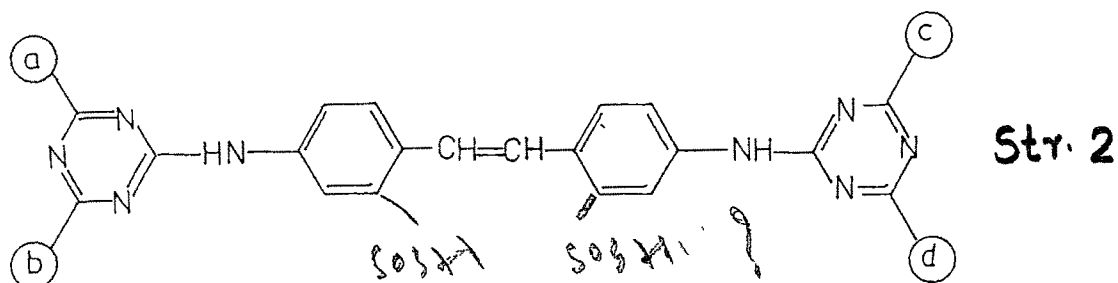
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The ability observed by ICI of the bisbenzoyl derivatives of Diamino stilbene to produce fluorescence on cotton and the marketing of 'Solium' started a intensive development which was further undertaken in Europe by the Geigy<sup>7</sup>, Sandoz<sup>8</sup> and Unilever<sup>9</sup> and in the United states by American Cyanamid<sup>10</sup>, General Aniline<sup>11</sup>, du Pont<sup>12</sup> and Procter & Gamble.<sup>13</sup>

This development began in 1935 when Hoffmann's Starkefabrik Ultrazell GmbH brought on to the market a washing starch whitened with umbelliferone acetic acid.

In 1940, Wenk and Eggert of IG - Farbenindustrie AG introduced derivative of 4,4' - diaminostilbene 2,2' disulfonic acid which still plays important role today. It was also during this period that the swisscompanies CIBA and Geigy started research in this field.<sup>1</sup>

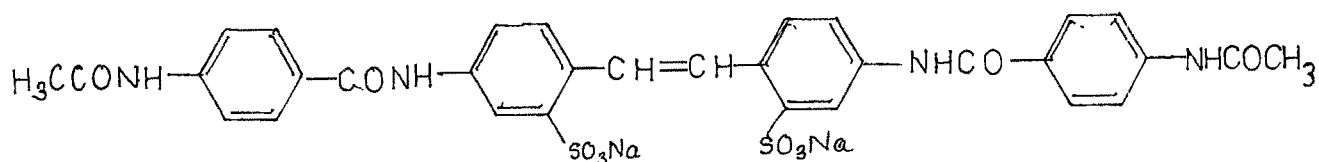
As a result of Wendt's discovery of the fluorescent 4,4' - bis triazinyl amino stilbene 2,2' disulfonic acid (3) compounds which are substantive to cellulose were prepared. These were mainly stilbene derivatives.<sup>13</sup>

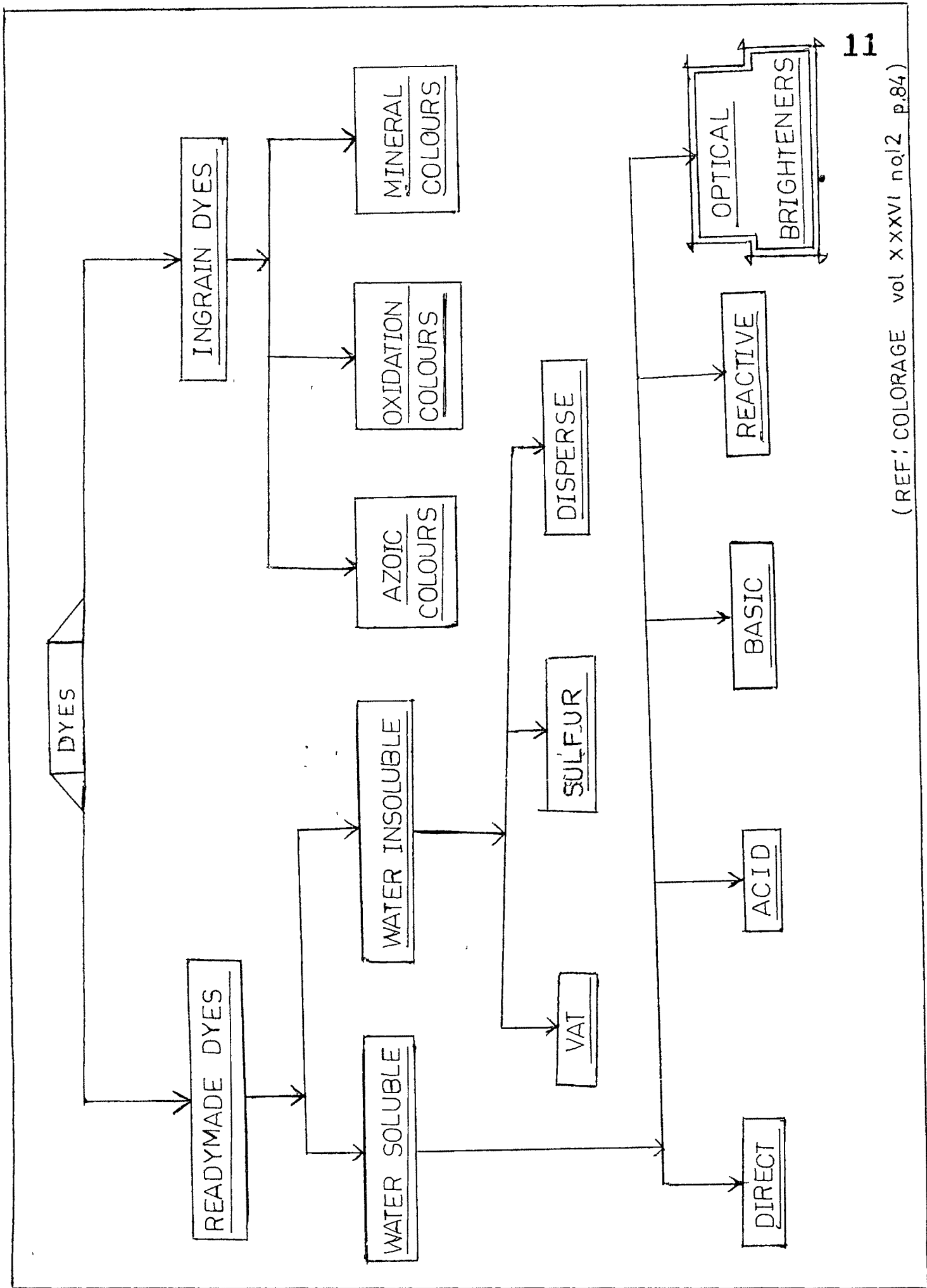


These stilbene derivatives are still components of today's over 80 % of the commercial products used for finishing textiles and are employed as additives to detergents<sup>14</sup> or used separately.

Such fluorescent brightening agents are used to achieve appreciable whiteness along with the brightness on the natural, semi-synthetic as well as synthetic fibers.

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