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INTER-SOCIETY COLOR COUNCIL

NEWS LETTER No. 57

JANUARY, 1945

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ANNUAL MEETING CANCELLED

In accord with advice received from the War Committee on Conventions, plans for the ISCC 14th annual meeting have been cancelled. This advice reached us after copy for the News Letter had been made up, as will be evident by reference to two later items that refer to plans that were already well under way when this happened — AAPL plans, and those of subcommittee on Problem No. 13.

Since the Government has taken this way to help reduce the very considerable amount of excess traveling that is overtaxing the capacity of our railroads and hotels we, as one of the groups involved, shall cheerfully comply — sorry though we are that it means cancellation of meetings that were to have been sponsored by member body groups. Perhaps some way can be found to circulate the AAPL papers for discussion, although visual aids to the presentation of such material are always best. It is expected that the reports of the subcommittee on Problem No. 13, and the report by H. L. Logan, intended for the Technical Session will be prepared in written form. Annual reports of officers, chairmen of member body delegations and of committees will be circulated by mail.

The News Letter is the medium by which the Council reaches its delegates and members, and since this copy goes out so soon after cancellation of the February meeting plans, it is sent by first class mail and will be the only notice of cancellation that you will receive.

NEW INDIVID- UAL MEMBERS

We welcome to individual membership in the Council the following persons elected by the Executive Committee as a result of a letter ballot on December 26, 1944: Ralph Harwood, Philadelphia Quartermaster Depot, who works with dyestuffs and textiles, and on the color problems at the Depot under the direction of Captain Backer; Hibbard S. Busby, 3517 Gillespie Avenue, Dallas 4, Texas, long interested in problems of color and well known to many Council members for his work in this field while research colorist at the Cheney Silk Company, 1915-23 (except war years). Mr. Busby is a charter member of the AATCC and for 11 years has been a member of the ASTM. He is particularly interested in color in relation to textiles and to motion pictures; the first is his business, the second his hobby (he has made 28 documentary Kodachrome motion pictures for the CCC).

WASHINGTON
AND BALTIMORE
COLORISTS

Mr. William H. Beck, individual member of the Council whose interest in color in philately is well known to many ISCC members, will be the speaker on February 5 at a dinner meeting of the Washington and Baltimore Colorists to be held at 6:30 P.M. at the YWCA Cafeteria, 614 E Street, N. W., Washington, D. C. Since 1929 Mr. Beck has made a very detailed study of thousands of stamps, both visually and instrumentally and by use of the Ridgway color book, used extensively by many of the old stamp writers. Mr. Beck's subject, "Philately and Color Research," will cover a description of the various methods of stamp collecting and its branches of research in history, usage, manufacture, collecting, cataloging, clubs and societies. In his study of the colors used and the reasons for their selection, he first used color charts for the determination and specification of these colors in conjunction with the Nickerson and Judd tolerance equations. Now much of the colorimetric data are obtained from spectrophotometric curves, and many of the descriptions are worded in terms of the ISCC-NBS system of color names. There will be a large display of stamps illustrating the various steps of this work. Any ISCC delegate or member who may be in Washington and wishes to attend should make his reservation promptly with Mr. Kenneth L. Kelly, Chairman of the Program Committee, at 2215 Constitution Avenue, Washington 7, D. C.

SUBCOMMITTEE ON
PROBLEM 13 MEETS

On January 10, a meeting of the subcommittee on ISCC Problem No. 13, A Study of the Illuminant in Textile Color Matching, was held in New York City to go over first drafts of the several papers intended for presentation at the Technical Session of the 1945 annual meeting. These papers will be the basis for a final committee report that should be ready by early spring. Committee members attending were: Captain Backer (assisted by Mr. Ralph Harwood) from the Philadelphia Q. M. Depot; Dr. I. H. Godlove, Chairman, AATCC Color Committee; Dr. E. I. Stearns, Calco Chemical Division; Mr. Constantin Monego, Julius Forstmann Co., Inc.; Miss Helen Greenler (for Mr. Frank J. O'Neil) of Pacific Mills; Mr. P. M. Otto, of Botany Worsted Mills; Mr. Frederick T. Simon, Sidney Blumenthal & Co.; and Miss Dorothy Nickerson, Chairman, U. S. Department of Agriculture.

NOTES ON
COLOR AND
ILLUMINANT

An epigram often flashes light into regions where reason shines but dimly.

-- E. P. Whipple

A flea-bitten fool made this foolish remark,
As he blew out the light: "They can't see in the dark."
-- Fuller, "Thesaurus of Epigrams," p. 123

Ignorance is the night of the mind; but a night without moon or star.
-- Confucius

Nature and Nature's laws lay hid in night;
God said, let Newton be, - and all was light.
-- Pope on Newton

I have nothing to ask but that you remove to the other side, that you may not, by intercepting the sunshine, take from me what you cannot give.
-- Diogenes to Alexander the Great, when the conqueror of the known world asked Diogenes what he would like to have.

AATCC The Color Committee of the American Association of Textile
 COLOR Chemists and Colorists met on January 11 at the Downtown
 COMMIT- Athletic Club, New York City, for consideration of its report
 TEE MEETS to the Research Committee of the Association, and other
 business. Eight of the ten members and three visitors were
 present; these included the members: Mr. Wm. D. Appel (President of the Society);
 Mr. K. H. Barnard; Dr. Carl Z. Draves; Dr. Edwin R. Laughlin; Mr. Constantin
 Monego; Mr. F. J. O'Neil; Dr. E. I. Stearns (vice-chairman); and Dr. I. H. Godlove,
 chairman; and visitors: Miss Helen Greenler, Miss Dorothy Nickerson, ISCC Secretary;
 and Mr. Bertil A. Ryberg. Absent were members Dr. Robert E. Rose and Mr. Frederick
 T. Simon.

AAFL PLANS FOR Sponsored by the American Artists Professional League, and
 DISCUSSION under the direction of Mr. Wilford S. Conrow, secretary of the
 SESSION AAFL and member of the ISCC Program Committee, plans have been
 completed for a Discussion Session of the 1945 annual meeting
 on Color From the Standpoint of the Artist. The program, as outlined by Mr. Conrow
 in a letter of December 31 to the secretary, will consist of the following:

Introduction and General Philosophy of Color, Wilford S. Conrow;
 The Artist Looks at Color, with demonstrations, John Scott Williams;
 "The Color Scale," William Churchill;
 What the Psychologists' Studies of Affective and Associative Psychology is Doing
 to Bridge the Gap between Artists and Scientists (this paper by distribution of
 printed copies), Hilaire Hiler.

Full outlines of the first three papers are already prepared and copies will be
 circulated to a number of Council members and others qualified to discuss them. If
 there are members who would like copies for this purpose, please advise the secre-
 tary. It is the hope of Mr. Conrow's group and of the ISCC Program Committee that
 these papers may serve as the nucleus for useful discussion. Having behind them
 the sponsorship of the American Artists Professional League, it is thought that
 these papers should represent the professional artists' point of view on color, and
 that prepared discussion will help to make the session of greater usefulness to the
 artist and scientist groups in the Council. The aim of the meeting is to form the
 beginning of a bridge that will help to close the gap that now exists between the
 color ideas of these two groups.

SAID OF AND BY A shoemaker should not judge above his shoes.
 THE PAINTERS -- Apelles (4th century B.C.)

Recollect that trifles make perfection, and perfection is no trifle.
 -- Michelangelo

The greatest man is he who forms the taste of a nation; the next greatest is he who
 corrupts it.
 -- Joshua Reynolds

No member needs so great a number of muscles as the tongue; this exceeds all the
 rest in the number of its movements.
 -- Leonardo da Vinci

That picture raffles will conduce to nourish
 Design, or cause good coloring to flourish,
 Admits of logic-chopping and wise-sawing,
 For surely lotteries encourage drawing.
 --Thomas Hood

J. GUILD HONORED Opposite page 1 in Proceedings of the Physical Society (London), vol. 56, part 1, no. 313, is the portrait of John Guild, twentieth Duddell Medallist. According to the citation, Mr. Guild, who is very well known to many color workers in this country, was born at Fauldhouse, Linlithgowshire, on the 16th of November, 1889. He was educated at Alan Glen's School, Glasgow, and at the Imperial College, London, where he spent 5 years as student and demonstrator in physics, the last two primarily with Prof. S. W. J. Smith in thermomagnetic work. He joined the staff of the National Physical Laboratory in April, 1914.

The twentieth Duddell medal has been awarded to him in recognition of his design of a number of optical and physical instruments of outstanding merit. The best known are his spectrophotometer (1924), the trichromatic colorimeter (1925), and the absolute radiometer (1937). Others are a spherometer of precision (1917), a very accurate angle comparator for the goniometry of prisms (1923), a flicker photometer (1923), a vector colorimeter (1925), an improved goniometric spectrometer (1926, with Mr. George Watts), a compensated thermopile (1931), and an instrument for evaluating the surface finish of metals (1940).

TCCA ELECTIONS At the 29th annual business meeting of the Textile Color Card Association of the U.S., Inc., held at the offices of the organization at 200 Madison Ave., New York City, on Dec. 7, 1944, the following directors were re-elected for the ensuing year: Waldo Grose, E. Irving Hanson, Allan C. Jacobson, Carl E. Kempf, W. R. MacIntyre, William B. Olmsted, Jr., Brainerd Pidgeon, Charles Pinnell, Armand Schwab, Alfred L. Simon, Roy E. Tilles, and John F. Warner. At a meeting of the directors held immediately after, the following officers were re-elected: President: Charles Pinnell; 1st Vice-pres.: Roy E. Tilles; 2nd Vice-pres.: Armand Schwab; Treasurer: Carl E. Kempf; and Secretary and Managing Director: Margaret Hayden Rorke.

For the year 1944 up to the date of the meeting, according to the report read by Mrs. Rorke, 304 new members were gained, as compared to 89 during 1943. In addition to expanded activities in South America, the Association gained new members in 8 foreign countries. Our available space does not permit detailing the activities reported. At the request of the Quartermaster General, the Association issued a supplement to its U. S. Army Color Card showing the Official Colors for Arms and Services. At the request of the Army, the Association issued a second edition of the U. S. Army Standard Card for the Official Shades of Olive Drab, Khaki and Drab Sewing Threads. There was also supplementation of the official flag colors of the United Nations and Latin American Republics. The Association cooperated with the Naval Medical Supply Depot in establishing color standards used for identification of medical supplies and services; and other similar cooperation was continued.

Mrs. Rorke stated that much progress had been made in the scientific work of the Research Associate, established by the Association at the National Bureau of Standards in Washington. This work includes the measurement, with the G. E. Recording Spectrophotometer, of the spectral reflectance of the 216 colors of the Ninth Edition Standard Color Card. When the entire data has been assembled, it will be published in booklet form as a supplement to the Standard Card. Mrs. Rorke expressed gratification over the success of the "timely color" themes launched by the Association and effectively promoted throughout the fashion industries. She also commented on the wide use of the Association's consultation service for members.

COLOR HELM We recently had passed on to us copy of a letter by an appreciative user of the Color Helm, a device for selecting harmonious colors, written to the producer, Fiatelle, Inc., by Michel Harritz, 320 Fifth Ave., Room 204, New York 1, N. Y. The letter reads:

Dear Sirs:

I am studying color at the Textile High under Mr. Pignard. I bought Four of your Color Helms; I have one set permanently on A, the second on B, the third set at C, and the fourth at D. I also bought a fifth one which I unmounted so as to see and compare all the colors represented.

When this war is over I intend to return to China to produce cross-stitch and petit-point and that is why I am studying color. I find the Color Helm very helpful and wonder how I got along without it for the last fifteen years that I spent at this work in China. I always wished there was such an instrument but never had the privilege of seeing one until I returned on the last Gripsholm and now I will never be without it. Obviously you were not represented in China and I would like to take this opportunity to propose to you a representation.

I also would like to know if you have any further literature on the application and the use of the Helm; or would you have a booklet reciting the names of the colors, tints and shades used on the Helm that could be adapted for specification of colors.

Any information or amplification on this subject will be highly appreciated.

(Signed) Yours very truly,
Michel Harritz

The editors may add that for some time Mr. Joseph P. Gaugler, of Fiatelle, Inc., has been an Individual Member of the Color Council. The new address of this company, who are color consultants and do color research and coordination, is Empire State Building, New York 1, New York.

SPECTROPHOTOMETRY OF PIGMENTS

A recent article on pigments is by our member Walter C. Granville, in Interchemical Review 3, 71-8 (Autumn 1944). The title is "Spectrophotometry in Evaluating Colorants."

This paper gives a general discussion of colorants, and is a companion paper to that published by N. F. Barnes in 1939 with spectral data on artist's pigments; for Mr. Granville's paper gives apparent reflectance curves for the following colorants: para red, toluidine red, barium lithol, red lake C, eosine lake, rhodamine lake 6G, Hansa yellow 10G, benzidine yellow, yellow lake, raw sienna, cadmium yellow, medium chrome yellow, phthalocyanine green, alkali green, dark chrome green, phthalocyanine blue, alkali blue, methyl violet, peacock blue, ultramarine blue, bronze blue, anatase titanium dioxide, rutile titanium dioxide, the yellow printing ink of the Interchemical Review cover, and a toned black printing ink.

BLACK BODY COLORS

A paper by H. G. W. Harding; Proc. Phys. Soc. 56, 305-28 (Sept. 1, 1944), is entitled: "Colours of Total Radiators Expressed on the C.I.E. Trichromatic System for the Temperature Range 1500-10-9000°K ($C_2 = 14384.8$)."

This paper contains tables of the colors of Plankian radiators expressed on the C.I.E. (or I.C.I) 1931 standard colorimetric system for the range 1500 to 9000° at 10° intervals, for 9500 to 11,000° with 500° intervals, and for 13333 1/3°, 20000° and 40000° K. and infinite temperature. The colors refer to energy distributions calculated from Planck's formula with the value of the constant shown in the title. Additional tables are included to facilitate the calculation of the colors if other values of the constant are used. The color differences are given for a change of the constant from 14384.8 to 14350 and from 14384.8 to 14320.

Another paper concerning black-body colors which is of much interest is one by E. Q. Adams and W. E. Forsythe, Denison Univ. Bull., J. of the Sci. Labs. 38, Dec. 1943, entitled "Radiometric and colorimetric characteristics of the black-body between 2800°K and 3800°K. This provides data for every 100° interval between these extremes which fills in between Skogland's highest and Moon's lowest temperature data, a number of tungsten-filament lamps occurring in this range. To be consistent with the data published by Judd (J. Opt. Soc. Amer., 1933), the authors have used $c_2 = 14350$.

NOTES ON
WHITE,
BLACK
AND GRAY

Everye white will have its blacke,
And everye sweet its soure.
-- Thos. Percy: Reliques; Sir Curline

Gray is the color of all theory.
-- Goethe

And finds with keen, discriminating sight,
Black's not so black -- nor white so white.
-- Canning: New Morality

In Tibur's sun, the nut-brown maid was told,
Ivory grows white though yellow turned and old.
Thither she hies her, but ere long comes back
(So strong the upland air) not blonde, but black.
-- Martial

The black crow thinketh her own birds white.
-- Gavin Douglas

SCOTOPIC
LUMINOSITY
CURVE

W. S. Stiles and T. Smith give a weighted mean recommended curve in Proc. Phys. Soc. 56, pt. 4, 251-5 (July 1, 1944); a mean scotopic visibility curve. The results of Hecht & Williams (1922), Stiles and Crawford (1934), Weaver (1937), Stiles (1939) and Walters & Wright (1943) are averaged, with the first and third determinations weighted by 3 and the others by unity. The quantity averaged was $\log S$, where S is the scotopic luminosity, having unit value at 510 mu. The ratio of scotopic luminosity (integral of $ES_d \lambda$) to photopic luminosity (integral of $EL_d \lambda$) is so defined that the two are equal at about 530 mu. If scotopic units are so chosen that scotopic and photopic values are identical for light of color-temperature 2360°K., the ratio by which photometric brightnesses, candlepowers, etc., must be multiplied to obtain scotopic values is $2.020 \times (\text{integral of } ES_d \lambda) / (\text{integral of } EL_d \lambda)$. The values of S and $\log S$ are given for 10 mu intervals from 370 to 790 mu. As indicated above, the early work of König & Ritter and of Abney & Watson is omitted in the average. The imperfections of the average are discussed, and the modifications with increase in brightness level.

1945 SPRING
HOSIERY
COLORS

Three lively sparkling colors captioned Sunlit Shades are highlighted in the Confidential Advance Hosiery Card for Spring 1945, which the Textile Color Card Association has recently released to its members. The new group, as announced by Margaret Hayden

Rorke, managing director, comprises Joytan, Sunniblush and Cheerglo. All colors, Mrs. Rorke stated, are "on the light side," and each has distinctive qualities that render it particularly appropriate with a wide range of smart costume colors, and they accord well with the 8 shoe colors approved by the joint committee of tanners, shoe manufacturers and retailers in cooperation with the TCCA. Literature of the

Association explains in detail how each of the three colors, small in number as a wartime conservation measure, can be combined with various other colors in the ensemble in a harmonious way.

1945 SPRING COORDINATION CHART OF WOMEN'S SHOE AND COSTUME COLORS

"Marching to Victory with Color" is the patriotic caption of this Chart, which the Textile Color Card Association has just issued to its members in the shoe and leather industry. Serving as a fashion and merchandising guide, this chart highlights in large leather swatches the women's shoe colors for Spring 1945, selected and approved by the joint committee of the Tanners' Council of America, the National Shoe Manufacturers Association and the National Shoe Retailers Association, in cooperation with the TCCA. These 8 colors comprise Town Brown, Army Russet, Bluejacket, Turftan, Liberty Red, Varsity Green, black and white. The small number of colors, explained Margaret Hayden Rorke, TCCA managing director, is due to the fact that, although color restrictions in Shoe Conservation Order M-217 have been removed, limitations of raw material and man-power still exist. The chart devotes a separate page to each shoe color and its smartest harmonizing or contrasting costume colors, the latter being portrayed in woolen and rayon fabric. Military and glove colors are also indicated.

COLOR TEMPERATURE OF TUNGSTEN LAMPS

On many occasions those working in color have need for information regarding the color temperature at which many usually available lamps operate at rated voltage. A recent article under the title "A Color Temperature Scale," by Dr. W. E. Forsythe and Dr. E. Q. Adams of the Lamp Department, General Electric Company, appeared in two parts in the September and October 1944 issues of vol. 47, General Electric Review, No. 9, 26-34, No. 10, 59-62. Part I: Lamp or furnace temperature is best determined by measuring specific brightness. These data, from General Electric laboratory tests, therefore, apply to a large number of the industrial arts. Part II: Color temperature and characteristics of various popular lamps.

It is probable that reprints of these two papers can be obtained by writing to Dr. Forsythe or Dr. Adams. In this connection we should also refer to an earlier and excellent report by the same authors, "The tungsten-filament incandescent lamp," Denison University Bull., J. of the Scientific Laboratories 32, 70-131, April 1937.

NOTES ON EYES AND VISION

Folded eyes see brighter colors than the open ever do.

-- E. B. Browning: A Child Asleep

I have a good eye, uncle; I can see a church by daylight.

-- Shakespeare

All seems infected that the infected spy,
As all looks yellow to the jaundiced eye.

-- Pope: Essay on Criticism, l. 568

COLOR NAMES

In the November Textile Colorist and Converter an article by Dr. Waldemar Schweisheimer is titled "Look What We Missed in Color Names." After speaking of the wide variety of color names, what the eye sees, and the fact that there are so many distinguishable colors, the article goes on to say that while the natives of some portions of the earth - for example, those who live in the Tundra - have no words for such colors as red, green and blue, they do have as many as 31 different words to differentiate

browns. The suggestion is made that this is due to the fact that they make their living from their cows which have a great many nuances of brown. The article goes on to say: "To the stranger the tundra seems a lifeless gray green or brown or green brown. It would be difficult or impossible for him to name and distinguish between more than ten colors there. On the other hand the native who lives continually in the tundra has some 500 to 800 words or word combinations to specify these colors." While we do not know the source of Dr. Schweisheimer's information, it sounds very plausible.

CLASSIFICA-
TION OF TYPES
OF VISION

We have received from Dr. Judd a list of classical definitions of the terms used to define types of vision together with a discussion of the terms proposed by Farnsworth in the November News Letter.

Trichromatism: a type of vision in which the colors seen require in general three independently adjustable primaries (such as red, green and blue) for their duplication by mixture. Normal vision is one form of trichromatism.

Dichromatism: a type of vision in which the colors seen require in general two independently adjustable primaries (such as red and green, or purple and yellow) for their duplication by mixture.

Monochromatism: a type of vision in which the colors seen require only a single adjustable primary to match them. Any light may serve as the primary.

Protanomaly: a type of trichromatism in which the luminosity function is too low at the long-wave end to fall within normal limits, and in which an abnormally large proportion of red in a red-green mixture is required to match a given yellow.

Deuteranomaly: a type of trichromatism in which the luminosity function falls within normal limits and in which an abnormally large proportion of green is required in a red-green mixture to match a given yellow.

Tritanomaly: a type of trichromatism in which an abnormally large proportion of blue is required in a blue-green mixture to match a given cyan.

Protanopia: a type of dichromatism in which red and bluegreen are confused, but no abnormal proportion of red plus green is required to match a given yellow, and the luminosity function is too low at the long-wave end to fall within normal limits.

Deuteranopia: a type of dichromatism in which red and green are confused, but no abnormal proportion is required to match a given yellow, and the luminosity function falls within normal limits.

Tritanopia: a type of dichromatism in which reddish blue and greenish yellow are confused.

Tetartanopia: a type of dichromatism in which blue and yellow are confused.

Achromatopsia: a type of monochromatism in which all colors are perceived as neutral (black, gray or white).

Comparison of these definitions with those proposed by Farnsworth reveal that his classification is based entirely upon chromaticity discrimination whereas the classical definitions involve chromaticity discrimination only in the limiting case to distinguish between trichromatism and the various types of dichromatism. There is

no necessary contradiction between the Farnsworth terms and the usual terms; and it may be instructive to enumerate the classical types included under each of the types proposed by Farnsworth.

<u>Farnsworth</u>	<u>Classical</u>
Normal	Normal, but some observers usually classed normal fail to qualify under Farnsworth's definition
Anomal	Probably either protanomalous, deuteranomalous, or tritanomalous, but might refer to some observers usually classed as normal
Monochromat	Achromat
Protan	Protanopic or protanomalous observers; but might also refer to a small proportion of observers usually classified either normal, deuteranopic or deuteranomalous.
Deutan	Deuteranopic or deuteranomalous observer; but might also refer to a small proportion of observers usually classified either normal, protanopic or protanomalous.
Tritan	Tritanopic or tritanomalous observer; but might also refer to a small proportion of observers usually classified as normal. Normal perception of fields affecting retinal areas subtending less than one minute of arc is tritanous.

It remains to be seen whether classification of observers on the basis proposed by Farnsworth is more useful than the classifications heretofore appearing in the literature, but it would seem that the Farnsworth classification ought to correlate more closely with ability of the observer to perform specific tasks requiring chromaticity discrimination. This classification accords with the philosophy of the red-green discrimination test developed for the Navy Department by the ISCC Committee under the chairmanship of Dr. LeGrand Hardy; see J. Opt. Soc. Amer. 33, 512 (1943).

SPECTRA OF MOLECULES A very recently published book which is worthy of a careful reading - indeed, we have read it through several times - is G. W. Wheland's "The Theory of Resonance and its Applications to Organic Chemistry;" 316 pp.; John Wiley & Sons, Inc., New York; \$4.50. Only chapter 6 is on "Resonance and Molecular Spectra," and is thus of special interest to our readers; but the whole book furnishes a fitting background for this excellent chapter. The concept of resonance has dominated modern chemistry since the idea of the shared-electron bond was introduced by G. N. Lewis. The book provides the most lucid general survey of the literature dealing with this concept that the writer of this review has seen. Though the chapter on spectra is disappointingly brief, we find in it a full diet of food for thought; and the book as a whole stimulates our appetite for the scientific pabulum originating in the field between physics and organic chemistry.

After defining quantum-mechanical resonance and stating the conditions of its occurrence, 8 pages are devoted to developing, in parallel columns, a "classical"-mechanical analogy to the quantum-mechanical system. To show that it is wrong to speak of resonance of a compound between two "forms," Wheland uses another characteristic analogy. "A mule is a hybrid between a horse and a donkey. This

does not mean that some mules are horses and the rest are donkeys, nor does it mean that a given mule is a horse part of the time and a donkey the rest of the time. Instead it means that a mule is a new kind of animal, neither horse nor donkey but intermediate between the two and partaking to some extent of the character of each. Similarly, the benzene molecule has a hybrid structure, not identical with either of the two structures first written by Kekulé, but intermediate between them. And it may be said that there are also smaller "contributions" from the so-called Dewar structures.

More important for our present discussion is the fact that in many molecules, essential contributions come not only from the electrically neutral molecules described by our classical organic formulas, but also from partially ionic forms involving "dipoles" in which there is a separation of positive and negative charges. Since this separation of charges involves the doing of (electrical) work, these "ionoid" structures (as Dilthey and as Wizinger call them) are of higher energy, that is, less stable, than the classical neutral structures. For the normal state of the molecule, the effect of resonance is to make the hybrid molecule more stable, that is, of lower energy. For the "excited" state, produced by the absorption of light, however, there is an increase of energy. Chapters are devoted to consideration of the nature of valence and the kinds of chemical bonds and to the determination of the magnitude of resonance energy in various types of compounds. It is explained that resonance between structures with purely covalent (shared-electron) bonds and those with purely ionic structures, leads to the existence of dipole moments; and conversely, moments can be used to examine the nature of the resonance.

In the chapter that is the real subject of this review, after the usual discussion of types of spectra, the Bohr relation between energy and frequency, and the relation of rotational, vibrational and electronic spectra, it is pointed out that the normal or "ground" state can often be described fairly accurately by a single (classical) valence structure; but the excited state usually requires a consideration of resonance among several structures, mostly ionoid. The latter often cannot be expressed at all by the conventional symbols.

A molecule like butadiene, a chain of 4 carbons joined by alternate single and double bonds (a relation we call "conjugated"), we find absorbs light of longer wave-length than that absorbed by an analogous compound with only single bonds. The actual molecule is a resonance hybrid, embracing chiefly the uncharged structure (of lowest energy), another with double bond in the middle and a "formal bond" between the terminal carbons, and other less stable structures with a positive charge on one carbon and a negative charge on another, these being of higher energy and lower stability. The ground state is made up largely of the first-named structure; but the first excited state is formed largely from the ionoid structures with charges or formal bond. These latter do not differ among themselves in energy, so resonance occurs among them and leads to considerable stabilization. The stability is greater than that in the ground state. Resonance thus leads to lower energy of excitation. Since, according to the Bohr condition, energy is inversely proportional to wave-length, absorption of light occurs at longer wave-lengths than if there were no resonance. Further, it may be seen that if the molecule is modified in such a way as to introduce more resonance (in the part of the molecular chain responsible for light absorption), as by introducing a so-called "auxochrome" group, then absorption may occur at still longer wave-lengths. This effect is known as the "bathochromic shift."

If we lengthen the carbon chain, and note that the first excited state may again be stabilized, relative to the ground state, by the resonance among ionoid structures,

we may expect this stabilization to be greater than in butadiene because of a larger number of possible structures. Consequently, the increase in the length of the chain (especially of the conjugated system) should result in a displacement of absorption to still longer wave-lengths, as it actually does.

The intensities, as well as the wave-lengths, of absorption, are affected by resonance. Thus, in butadiene, the intensity per double bond is greater than in ethylene (with one double bond between the 2 carbons). This high intensity has been related theoretically (Mulliken, 1939) to the effect of structures with high dipole moments, the ionoid structures with separated charges (dipoles), which make the main contributions to the first excited state (and small ones to the ground state). Similarly, the intensity of absorption in the "condensed" hydrocarbons, made up of benzene rings fused together, increases, per benzene ring, with the number of rings.

Intense absorption also occurs when, as in dyes like crystal violet, an ionic charge occupies different positions in the various resonating structures. This was shown (Pauling, 1938) to be due to the marked difference in the distribution of charge in the various structures. Many dyes are salts in which this condition is true in the colored cations or anions involved in the resonance. But the base of crystal violet has restricted possibilities of resonance, and accordingly is colorless. In strongly acid solution the violet dye adds on a proton, assuming a double positive charge, with possibilities of resonance like those of the dye malachite green. Accordingly, it becomes green.

But it is pointed out that an ionic charge is not a prerequisite for dye character, as we may see in the neutral molecules of indigo. The characteristics of such dyes can be seen in the experiments of Brooker and his co-workers at Eastman Kodak, and especially in the (1942-3) work of Sheppard and his co-workers at Kodak on the effect of solvents on the spectra of these dyes. The wave-length of maximum absorption, of a certain neutral dye, varies from 552 mμ in cyclo-hexane to 668 mμ in water. This trend toward longer wave-length with increasing dielectric constant of the solvent (and therefore less work involved in displacing charges) has been explained as a result of an increasing stability, and hence an increasing contribution, of the ionic structures (whose resonance is presumably responsible for the color) in the more polar solvents. On the other hand, a very similar dye which has its most important resonance among nearly equivalent structures without separation of charges, shows hardly any effect of solvents.

Brooker compared the dyes resonating among structures of similar stability (e.g., the green and the violet), and those like indigo resonating among structures differing greatly in stability (and energy), and solvent-sensitive. This work we have recently reviewed in these pages.

More quantitative treatments than that indicated here, and based on quantum mechanics, have been given by several workers (Sklar, 1937; Förster, 1938; Pauling, 1939; Mayer & McCallum, 1942; Herzfeld & Sklar, 1942). Although the calculations of Sklar and Förster ignored the structures with ionic bonds and considered only purely covalent ones, their results are very interesting and instructive.

An important factor, which we have already touched upon in reviewing the work of Hodgson, is that a planar structure appears to be necessary for the full development of resonance (Rodebush & co-workers, 1940-1; R. N. Jones, 1941). Two benzene rings when conjugated normally are coplanar and absorb more intensely (per ring) than a

single ring. When large groups are introduced near their point of junction, they are forced by repulsive forces into different planes; and accordingly the conjugation effect on absorption vanishes. It is an interesting fact, whose explanation our available space does not permit, that this effect of inhibition of resonance decreases the intensity more pronouncedly than it changes the wave-length of maximum absorption.

Returning to the explanation of intense color in dyes, it may be said that on page 1982 in Pauling's chapter of Gilman's "Organic Chemistry," the excellent argument given there is summarized by saying that "intense color results from resonance between two equivalent or nearly equivalent structures with which a large dipole moment is associated (the actual electronic transition being between resonating structures formed from these). Nitrogen and oxygen atoms are important in dyes in order to introduce large electric (dipole) moments."

ABSORPTION SPECTRA AND SOLVENTS

Two more papers on the effect of solvents on the absorption spectra of dyes by S. E. Sheppard and his co-workers at Eastman Kodak continue the extensive work reported in 1942 (J. Amer. Chem. Soc. 64, 2923-37, 2937-47; also Rev. Mod. Physics 14, 303-40; 1942); these

papers are in the December, 1944, Journal of the American Chemical Society. Although the specific problem was that just stated, the principles utilized and the implications of theory and empirical fact are broader in scope and interest than this subject; and the papers are full of suggestions for other workers having to do with the color of dyes.

The effects of solvents in modifying absorption bands may be attributed to the so-called "Van der Waals forces," or non-chemical-valence forces, of three types: (1) the "orientation" effect of electrostatic interaction of permanent dipoles, first studied by Keesom; (2) the Debye effect of induced dipoles; and (3) the London-Margenau "dispersion effect," a quantum-mechanical influence due to the mutual inductance of electron clouds. Effect (1) depends on the dipole moments of the solvent and the dissolved dye, and is temperature-dependent. Effect (2) depends on a lower power of dipole moments and on the polarizabilities (susceptibilities to electron displacement), and is only slightly affected by temperature change. Effect (3) depends on polarizabilities and the characteristic frequencies contained in the classical dispersion formula. Calculations for a number of simple molecules proved effect (3) to be of greatest magnitude, and (1) frequently of considerable size, while (2) is usually negligible. The distinction between the three types of interaction effect, however, is primarily historical and a matter of convenience only, the forces being fundamentally of the same nature; they correspond to summation of large or small energy differences involved in different types of spectra (rotational, vibrational or electronic). To a first approximation these forces vary inversely as the sixth power of the distance, though more accurate calculations, involving dipole-quadrupole and quadrupole-quadrupole forces, occurring along with dipole-dipole forces, include higher inverse powers of the distance of separation of poles. The first two effects are important only for polar molecules, while the London or dispersion forces act between non-polar molecules also, and are temperature-independent.

The dispersion effect is involved in the earliest stated rule dealing with the effect of solvents; this was the rule of Kundt (1874), according to which the absorption band is displaced toward longer wave-lengths by increase in dispersion (or refractive index) of the solvent. Apparent exceptions were later found; but Sheppard et al find that the rule holds well if limited to non-polar solvents.

Dispersion forces may also be involved in the greater (bathochromic) wave-length shifts due to aromatic solvents compared with aliphatic solvents of the same chemical type and dipole moment; also in the increased shift in going from alkyl chloride to bromide to iodide as solvent. Probably there is a small but increasing Debye induction effect on polar molecules dissolved in non-polar solvents of increasing dielectric constants.

In a homologous series of polar solvents, of a given chemical type, the bathochromic shift in wave-length is constant. But when we change from a solvent of one type to others of increasing dipole moments, as in going through the solvent series: hydrocarbon to ether to alkyl acetate to ketone to nitro-compound, the shift to longer wave-length increases. This is presumably the Keesom effect. Polar character appears to reduce the shift corresponding to a given refractive index. "Associating" polar solvents (fatty acids, alcohols and amines) act as if they have effectively greater moments, as compared to the individual molecules of their vapors.

Most dilute solutions in organic solvents such as alcohol obey Beer's Law, as if they were molecularly dispersed. In water, on the other hand, minor (beta and gamma) bands appear at shorter wave-lengths, gaining with increasing concentration at the expense of the main (alpha) bands. There are two schools of thought as to the nature of the secondary bands. Most workers are agreed that in concentrated solutions aggregated (dimeric and possibly polymeric) molecules exist along with the monomeric dye molecules present in alcoholic, diluted or heated solutions. Some workers (Scheibe, Rabinowitsch, W. C. Holmes) believed that the reversible transition of monomers to dimers is governed by the chemical mass-action law. But Sheppard believes that two molecules of dye solute are held by definite forces to a molecule of water. According to him, the secondary bands are due to an increased probability of coupling of vibrational with electronic energy.

The effect of increased hydrogen-ion concentration (from acids) is often the addition of a proton, producing a new species with a modified absorption band at longer wave-lengths ("halochromy"); but sometimes there is "reversed halochromy." Solution in concentrated sulfuric acid may add on two protons, and, by blocking the resonance responsible for the color, discharge the color. Resonance-stabilized compounds, such as benzene, are in general insensitive to solvent effects. The Keesom and Debye effects, but not the London dispersion effect, are likewise limited for ionized and symmetrical dyes.

If we consider, instead of the effect of a solvent molecule on a dissolved dye molecule, the influence of two similar dye molecules on each other, we find that the interaction energy is proportional to the square of the polarizability (which can be readily calculated from bond-refraction data) and to the characteristic frequency. On the basis of a simplified model, this can be put in the form $f^2 \lambda^3$. For the meaning of these terms, see our March, 1944, review of the work of Neale and Stringfellow (News Letter No. 52), confirmed by the reviewer: λ may be taken approximately as the wave-length of maximum absorption. Whenever the dye is deeply colored, these quantities are large; and in these cases we may expect considerable interaction or aggregation, consequently also deviations from Beer's law. In fact, it can be easily shown that the interaction between two dissimilar molecules A and B is always less than the harmonic mean of the individual interactions of A with A and B with B; and since we know from Neale and Stringfellow's report of large interactions of the A-B type, it follows that the A-A and B-B type of interactions may be large. And the entrance of λ as the third power leads us to expect more interaction (Beer's law deviation, aggregation effects and in general more "spectral anomaly") of green and blue dyes than of reds and yellows.

The importance of these results in their bearing on spectrophotometric analysis, dyeing and studies of the correlation of physico-chemical structure and properties of dyes, will be immediately obvious to most of our readers and will need no further comment.

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