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THE JOURNAL OF THE SOCIETY OF COSMETIC CHEMISTS

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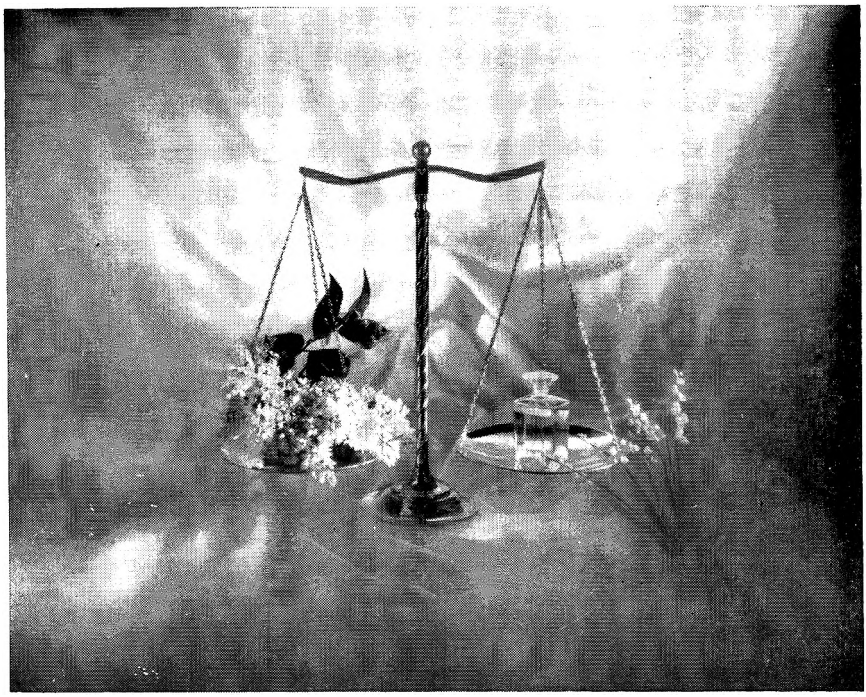

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VOLUME XIV • NUMBER 5

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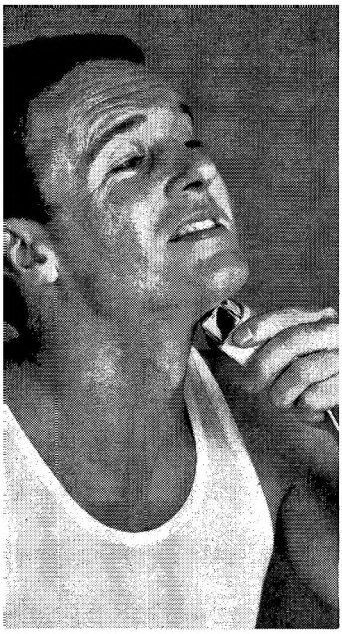

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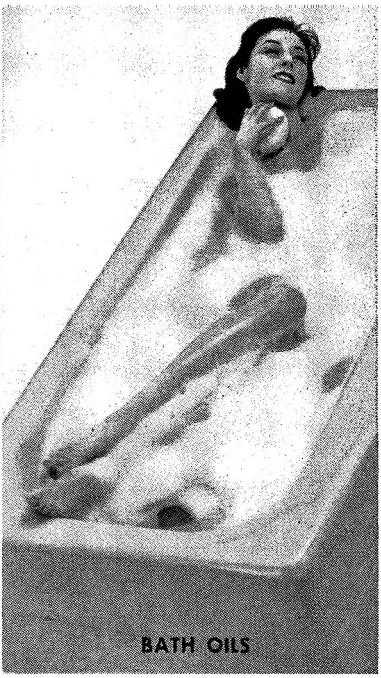

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at

COLUMBIA UNIVERSITY
NEW YORK CITY
June 22–26, 1964

For details about the Scientific Program, Registration Fees and the form for making proposals for the Scientific Program, see page xvii of the March 1963 issue. Additional facts about the 1964 IFSCC Congress appear on page 113 of the February 1963 issue of the SCC Journal.

Those who wish to reside on the Columbia University Campus during the IFSCC Congress in June 1964 are urged to mail the attached reservation card by June *1963*. The Arrangements Committee can then make the required guarantees to Columbia University. The $25.00 deposit will be refunded upon request up to May 15, 1964.

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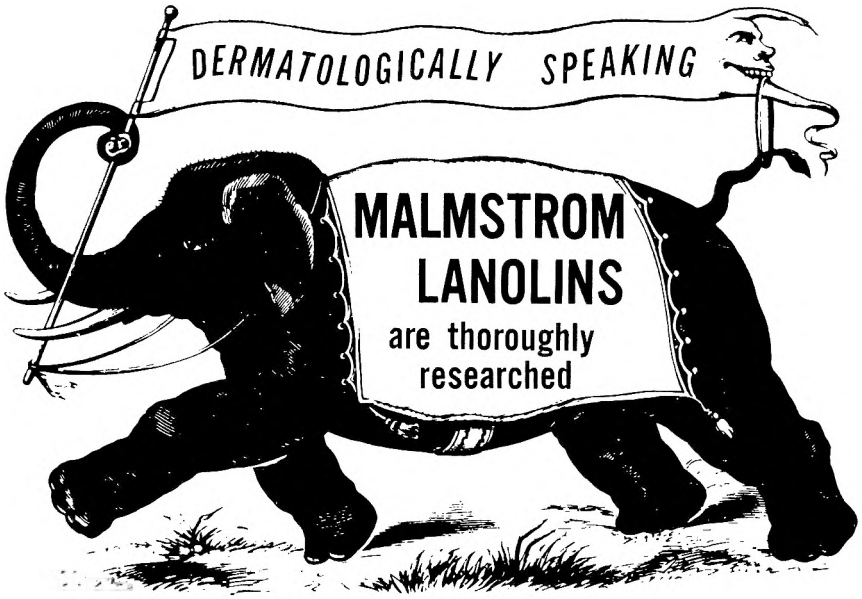

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THE NINTH SPECIAL AWARD

May 8, 1963

Hotel Biltmore, New York City

DR. JEROME GROSS of Massachusetts General Hospital and the Harvard Medical School is this year's winner of the Society's annual Special Award. He was awarded the honor for his pioneering studies on the formation of collagen.

Dr. Gross completed his undergraduate work at the Massachusetts Institute of Technology and obtained his M.D. degree from New York University in 1943. After his internship at the Long Island College Hospital, he served as a medical officer in both the European and Pacific theatres of operation during and after the war. In 1946 he joined the staff of the Biology Department at M.I.T. In 1955, he joined the Department of Medicine at Harvard Medical School, establishing his laboratory at the Massachusetts General Hospital. He is now head of the Biology Laboratory of the Lovett Memorial Group for Study of Diseases causing Deformities at the Massachusetts General Hospital and Assistant Professor of Medicine, Harvard Medical School.

Primarily known as a medical biologist, Dr. Gross has published a number of studies on the composition, structure, function, genesis, reactivity and abnormalities of connective tissue. Those papers which determined the Society's choice for this year's Special Award are listed at the end of this notice.

The Special Award is presented each year to the author or authors of the report(s) of basic research, published in the past two years, judged to be of the greatest potential value to cosmetic technology.

The 1963 Special Award was presented to Dr. Jerome Gross at the Society's annual May meeting, this year held jointly with the American Medical Association at the Hotel Biltmore on May 8, 1963. Dr. Thomas B. Fitzpatrick, head of the Department of Dermatology at Harvard Medical School, acted as eulogist for Dr. Gross.

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EUROPEAN TRAVEL ARRANGEMENTS IFSCC CONGRESS

New York

June 22–26, 1964

The British and German Societies of Cosmetic Chemists are planning to charter jet aircraft for those European members desiring to attend the 1964 IFSCC Congress in New York. The fares from London to New York and return will be approximately $210, and from other European cities, approximately $238 to $252 per person, irrespective of age.

The proposed departure from London is on the morning of June 21, 1964, thus arriving in New York during the afternoon. The return flight is scheduled to leave New York between July 5 and 12, 1964, depending on the wishes of the majority of the participants.

Participants must also return as a group and the free baggage allowance is 44 lb. All rates are subject to confirmation because the 1964 trans-Atlantic fares structure will not definitely be known until the autumn of 1963.

Anyone interested in coming to the Congress is asked to complete the post card inserted in this issue of the JOURNAL or to communicate with either of the following:

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ULTRAVIOLET ABSORBERS AS STABILIZERS IN THE COSMETIC INDUSTRY

By M. R. Leibowitz and F. B. Lane*

Presented December 4, 1962, New York City

Abstract

Ultraviolet radiation is primarily responsible for the degradation in sunlight (and in fluorescent light) of many chemicals, plastics, oils, fats and colorings. In the cosmetic and pharmaceutical industry this degradation is of great concern, and it is necessary to use stable broadly absorbing ultraviolet absorbers in order to protect both the product and the substrate such as skin, hair, etc.

Ultraviolet absorbers of the type currently used in suntan lotions are not satisfactory for use as stabilizers in preventing degradation. They are purposely designed to absorb in a narrow range (not above 310 to 320 millimicrons) and have rather poor light fastness. To date, only three classes of compounds have been found which are strong UV absorbers and are stable in a compatible medium. These classes are: (a) 2-hydroxybenzophenones (including salicylates); (b) 2-hydroxybenzotriazoles; and (c) substituted acrylonitriles.

Most colors used in the cosmetic industry do not have a high degree of stability under the influence of UV and visible wavelengths (350 to 450 millimicrons). Accordingly, stabilizers, which absorb strongly in this region, are necessary to protect cosmetic products. Factors influencing the choice of a suitable absorber for use as a stabilizer in any specific application are discussed. In addition, methods of use and the latest available absorbers are reviewed.

Ultraviolet (UV) radiation, though comprising only 5% of the radiant energy reaching sea level from the sun, is chiefly responsible for the degradation of many chemicals, plastics, oils, fats, colorings, perfumes, etc. Of course, it should be recognized that there are other sources of degradation besides UV light, such as oxidation, heat and ordinary visible light. Since a UV absorber will protect only against UV degradation, often a combination of stabilizers is necessary to satisfactorily safeguard a product. However, UV light is in many cases the major cause of degradation. It can either initiate a decomposition that then proceeds by another mechanism such as oxidation, or it can be absorbed as UV energy and be directly responsible for the decomposition.

In both types of degradation, a proper UV stabilizer will prevent this decomposition to a large degree. Members of the cosmetic and pharmaceuti-

* Antara Chemicals, Acetylene Chemicals Dept., Div. General Aniline & Film Corp., New York 14, N. Y.

cal industry who are greatly concerned over the stability of their products when exposed to sources of UV radiation, such as sunlight or fluorescent tubes, are finding the use of UV absorbers convenient as stabilizers for both the product and the substrate, e.g., hair and skin.

It can be demonstrated that a broadly absorbing UV absorber, when used in proper concentration in a filter, can screen out all of the UV portion of the spectrum. It is then obvious that the ideal way to protect products from UV degradation is to have some means of filtering out all of the UV light before it hits the material which will decompose. Unfortunately, it is not always possible to achieve this in practice.

There are many substances which will absorb UV light, but only a few of them are satisfactory stabilizers. For example, many organic substances will absorb UV light, but practically all of these will be decomposed by UV energy. Some substances, such as optical brighteners, are very strong absorbers of ultraviolet radiation but convert this energy into visible light and thus are stable for relatively short periods of time. Of course, the cosmetic industry is well acquainted with suntan lotions, which were amongst the first products to utilize UV absorbers. However, the chemical structures of compounds currently used in ordinary suntan lotions are not satisfactory as UV stabilizers, since they are purposely designed to absorb within a narrow wavelength (290 to 310 millimicrons) and do not absorb in the region which causes most damage to cosmetic products. Also, it is not necessary, as reported by Gantz and Roberts (1), for suntan type absorbers to have good UV light stability. Actual tests in our laboratories have demonstrated that many of these products lose as much as 50% of their ability to absorb UV light after only several hours exposure in a Fadeometer.

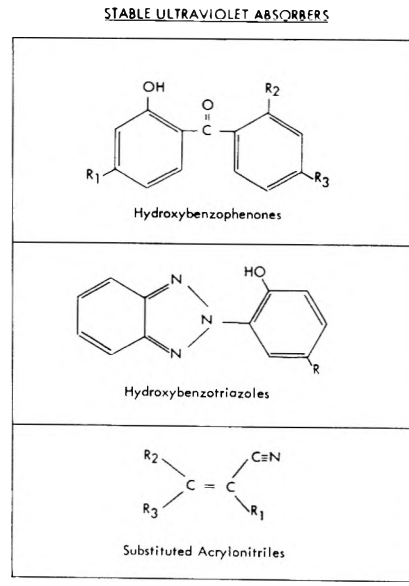


Figure 1.—Basic chemical structures that are strong UV absorbers and stable to long exposure to UV light.

To date, only three chemical structures have been found which are both strong UV absorbers and stable to long exposure to UV light (at least several hundred hours in the Fadeometer). These absorbers function as stabilizers by absorbing UV light, which is dissipated as harmless infrared energy. The absorber itself, when properly dissolved in a compatible

medium, is not decomposed and continues to act as a stabilizer for the substance requiring protection.

Figure 1 shows the basic chemical structures of these absorbers: (a) 2-hydroxybenzophenones, (b) 2-hydroxybenzotriazoles and (c) substituted acrylonitriles. The benzophenones, or salicylates, were the first to be found useful. The salicylates have an alkyl group attached to the carbonyl group through oxygen, whereas the benzophenones carry aromatic groups. The salicylates generally have weak absorption properties and do not absorb in the near UV where most degradation occurs. The R-groups on the benzophenones can be OH, alkoxy, halogen, or H groups, and a large number

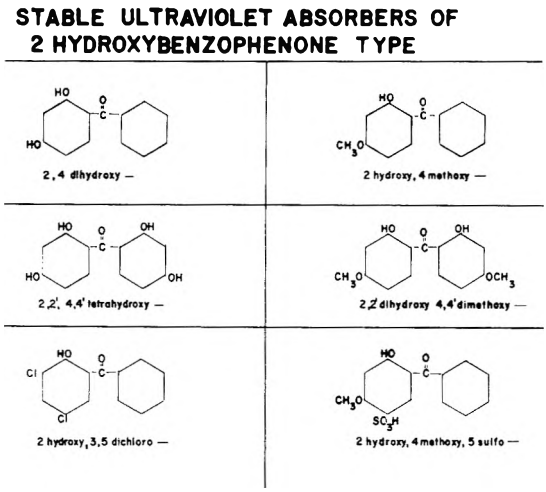
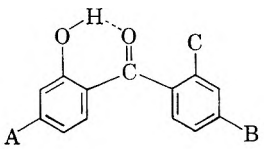


Figure 2.—Examples of various 2-hydroxybenzophenone derivatives that have been commercially available.

of such derivatives have appeared commercially or have been synthesized on an experimental basis. The 2-hydroxybenzotriazoles were produced commercially several years ago; R represents an alkyl group. The substituted acrylonitriles are the newest class of stable UV absorbers; the R group can be alkyl or aryl groups containing various substituents.

Figure 2 shows a number of stable UV absorbers of the benzophenone type, which have been supplied commercially. The compounds are examples of the various derivatives of 2-hydroxybenzophenone that can be synthesized. Each of these materials is a stable UV absorber but has different solubilities, compatibilities and absorption characteristics. Table I compares such a homologous series of ultraviolet stabilizers with respect to absorption characteristics and solubility. The E-value is a measure of absorption at a specific wavelength for a specific concentration and path length, while T_{50} is the wavelength at which 50% transmission is ob-

TABLE I—COMPARISON OF A HOMOLOGOUS SERIES OF UV STABILIZERS WITH RESPECT TO ABSORPTION CHARACTERISTICS AND SOLUBILITY*



BASIC FORMULA (I)

Chemical Name	Substituents on Basic Formula A	B	C	E† 350mμ	E† 370mμ	T_{50}‡ mg./100 ml. Absolute Methanol 2.5	25.0	250	Solubility, % by wt. Ethyl Acetate	Toluene
Monosubstituted Derivatives of Basic Formula										
1. 2,4-Dihydroxybenzophenone	OH	...	...	32	7	360	384	404	25	<1
2. 2-Hydroxy-4-methoxybenzophenone	OCH_3	...	...	32	9	360	384	404	28	52
Trisubstituted Derivatives of Basic Formula										
3. 2,2′-Dihydroxy-4,4′-dimethoxybenzophenone	OCH_3	OCH_3	OH	41	23	384	409	427	5	5
4. 2,2′,4,4′-tetrahydroxybenzophenone	OH	OH	OH	57	32	384	409	427	20	<1
5. Mixture of (3), (4) and related isomers	...	...	...	45	26	384	409	427	10	<1

* Absorbance and solubility data are average readings since slight variations are observed with different commercial lots.

†Specific Extinction Coefficient = $E = \frac{\text{Optical density}}{c}$; 1 cm. quartz cell, c = 1 g./liter in methanol, Beckman DU.

‡ T_{50} = wavelength in mμ at which 50% transmission is observed, Beckman DU; T_{50} is frequently called "cut off" and is used as a convenient means of referring to the max. wavelength at which UV protection is afforded under a given set of conditions.

served. As the table shows, the monosubstituted derivatives of Formula I (disubstituted benzophenones) have almost identical absorption characteristics but considerably different solubilities. On the other hand, the trisubstituted derivatives of Formula I (tetrasubstituted benzophenones) all have considerably stronger absorption at the longer wavelengths than the monosubstituted derivatives. Again, within themselves they have similar absorption but widely different solubility properties. It should be noted also that, as concentration is increased, the wavelength of 50% transmission is shifted closer to the visible. However, because of the stronger absorption of the trisubstituted derivatives, one can obtain equivalent absorption at one-tenth the concentration of the monosubstituted compounds.

Figure 3 shows the difference between the absorption curve of a disubstituted benzophenone and that of a tetrasubstituted benzophenone. It

can be seen that at equal concentrations the tetrasubstituted benzophenones absorb much closer to the visible and will screen out a greater amount of UV light, particularly in the wavelengths closer to the visible where much degradation occurs. Figure 4 shows how the transmission curve of a benzophenone will vary with concentration and, at increasing concentrations, the curve is shifted toward the visible.

The hydroxybenzotriazoles and substituted acrylonitriles are relatively new materials and have not yet realized their potential in the cosmetic industry. The acrylonitriles have recently been investigated by Rossman, Knox and Freeman (2) as a means of preventing UV degradation of the skin and were found to be adaptable to dermatological use as topical sun screens. At present only a limited number of hydroxy-

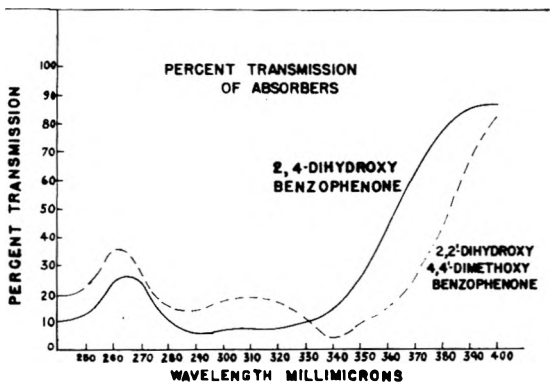


Figure 3.—Comparison of absorption curves, at a level of 0.025 g/liter, of a disubstituted and tetrasubstituted benzophenone. (The tetrasubstituted derivative absorbs closer to the visible).

benzotriazoles and substituted acrylonitriles are available, but many more are being developed in various research laboratories. The substituted acrylonitriles are extremely light in color and are completely unreactive toward salts, high pH and metallic substances. On the other hand, the benzophenones are sensitive to pH, metals and other materials which will react with the hydroxy group. The absorption properties of both the benzophenones and benzotriazoles depend upon the presence of hydroxy groups; therefore, any system which can react with the hydroxy groups will considerably alter their absorption characteristics. On the other hand, because the substituted acrylonitriles do not require hydroxy groups for absorption, they offer great promise as stabilizers with wide compatibility.

Of particular concern to the cosmetic chemist is the method of using these stabilizers in order to protect a product or a substrate, such as skin or

hair. First of all, one must determine if the problem of degradation is due to UV light. This can be done by a very simple method, developed by Holmes and Signore (3), in which a clear cellulose acetate film, containing a broadly absorbing UV absorber in the proper concentration, is used to screen out all UV light up to 400 millimicrons. This filter enables one to determine if the problem is due to UV degradation or to some other form of degradation, such as heat, oxidation, or visible light. As mentioned earlier, in some cases a combination of stabilizers is desirable. For example, if UV light initiates the formation of free radicals, and these radicals are then oxidized, a combination of an absorber and an anti-oxidant is more efficient than either stabilizer alone. The degradation of products by UV light often results in fading of colors, precipitate formation, development of foul odors, etc. The cosmetic chemist is interested in avoiding this degradation, so that his product will not be destroyed and its efficiency will last.

There are two possible methods of protecting a product from UV degradation. The first, and more efficient method, is to screen out completely the UV light before it hits the product. This can be done by incorporating the stabilizer in some form of screen, such as in a coating on a glass bottle or by incorporation directly into a plastic container, such as polyethylene or polystyrene bottles, or the product can be wrapped in a clear film containing the absorber. For example, tests show that a proper stabilizer incorporated into a PVC coating on a glass bottle can prevent the fading of a red color after one hundred hours' exposure in a Fadeometer. Unfortunately, it very often is not practical to use the absorber in this manner; in most cases the stabilizer is incorporated directly into the product. This, also, is an efficient method of protecting the product, and often as little as 0.05% of a proper absorber is enough to give satisfactory stability. In the case of clear solutions, incorporation of the absorber directly in the solution is often just as satisfactory as a filter. However, in the case of opaque products such as creams and lotions, the problem of protection is more complicated; here

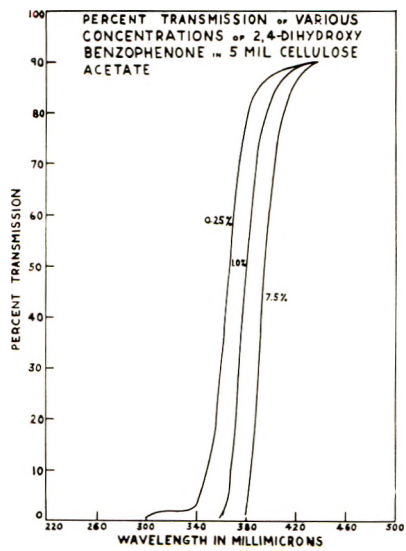


Figure 4.—Comparison of absorption curves, at varying concentrations, of a disubstituted benzophenone. (Increasing concentration shifts the curve toward the visible.)

an outside filter is usually more efficient than direct incorporation.

No matter which method is used, a number of factors determines the choice of stabilizers. Unfortunately no single stabilizer has yet been found that will solve all problems, so a specific stabilizer has to be chosen for each particular application. The following factors should be kept in mind when deciding which absorber to use:

1. *The ultraviolet wavelength to which the product is sensitive*—In the case of cosmetics this is usually in the area of 350 to 450 millimicrons. Accordingly, an absorber is necessary that will absorb strongly close to the visible, and even partly into the visible region. This is particularly important because most colors which are permitted by federal regulations do not have a high degree of stability in the presence of UV and visible wavelengths. These colors degrade rapidly in the region close to the visible, and accordingly an absorber with peak absorption as close to the visible as possible is desirable.

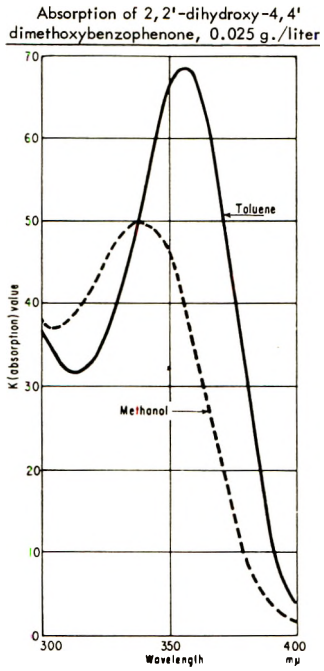


Figure 5.—Shift of absorption curve toward the visible with decreasing polarity of solvent.

2. *Solubility*—In order for an absorber to act effectively as a stabilizer it has to be soluble in the system in which it is used. The type of solvent used will also affect the absorption curve of each absorber. The curve is shifted toward the visible in going from a polar solvent to a nonpolar solvent, the effect being most marked in the case of 2,2′-dihydroxy-4,4′-dimethoxybenzophenone. Figure 5 shows the curves of this absorber in a polar solvent, such as methanol, and in a less polar solvent, such as toluene.

A suggested explanation for this unusually large shift is that in toluene this compound assumes a completely co-planar (and therefore more conjugated) configuration. In hydroxy solvents, one chelate ring is broken by chelation of the carbonyl of the absorber with the hydroxy solvent. In addition to this effect on absorption characteristics of the solvent, if the absorber is not dissolved in the system, it will not function as a stabilizer. In fact, if the absorber precipitates out of solution or exudes out of a film it is very rapidly degraded and will last only a very short time (4). On the other hand, if it is soluble, it can last for very long periods

of time without decomposition. Absorbers that are soluble in different solvents, including water are commercially available.

3. *Compatibility*—The absorber has to be compatible with the ingredients of the system. If it reacts with the materials in solution, it may lose its efficiency. For example, alkaline pH will reduce the efficiency of hydroxybenzotriazoles and hydroxybenzophenones. If the absorber is used in a coating on a glass bottle or in a plastic film or bottle, the absorber must be compatible with the polymeric material used so that it does not exude out of the film. Moreover, the thermal and chemical stability of the absorber must be taken into account for any specific conditions the product may meet.

4. *Concentration*—In order to stabilize effectively against UV degradation, a certain minimum concentration of absorber is necessary. This concentration varies with the thickness of the material in which the absorber is incorporated. In the case of clear solutions, low concentrations by weight are often satisfactory, because of the large amount of absorber present throughout the depth of the bottle. In the case of thin coatings, higher concentrations of absorber in the coating are necessary because of the relatively thin layer of film.

In addition to the above most important factors, very often color of the absorber and, of course, toxicity or dermatological effects of the absorber are also critical. Gantz and Roberts (1) reported most of the commercially available absorbers do not cause skin or eye irritation and have low orders of toxicity under ordinary use conditions. These absorbers appear to be satisfactory for topical applications, since they do not cause skin irritation in effective concentrations. Regarding color, it should be realized that the closer to the visible presently available stabilizers absorb, the more yellow they may appear.

In addition to protection of the product, the cosmetic chemist is often interested in protecting a substrate, such as natural hair, dyed hair, skin, etc. All these materials are sensitive to UV light and can be protected from UV degradation with the proper use of UV absorbers. Of course we all know of the effects of UV light on skin, and recent medical work by Knox (5) and others in this area has demonstrated that UV light is the major cause of skin aging, wrinkling and possibly even skin cancer. These workers (6) have urged the use of broadly absorbing UV absorbers, such as discussed in this paper, in everyday cosmetics in order to continually protect the skin against UV radiation. Knox (7) demonstrated that 3-benzoyl-4-hydroxy-6-methoxybenzene sulfonic acid was the most effective absorber in preventing this degradation. The reason for the efficiency of this absorber may be that it is substantive to skin and thus gives a greater amount of coverage and protection. In fact, Rose and co-workers (8) found that this same absorber was most effective in preventing the yellowing of wool by UV

light and compared their work with Knox's. Since wool and skin are similar in many respects, the substantivity of this water-soluble absorber to these materials would appear to be a factor.

Hair can be protected from UV degradation in several ways. The absorber can be incorporated into a hair spray or wave set so that, when applied to the hair, a film containing the absorber will protect the hair. Or the absorber can be incorporated into hair tints and, when the tint is applied to the hair, the absorber will stay in the coloring material to prevent fading of the color. The absorber can also be incorporated into shampoos for use on hair. In this case it is preferable to use a shampoo that leaves a film on the hair to give the hair greater manageability. Such a film will act as the medium for the absorber (9).

A number of absorbers which can be used as stabilizers are commercially available under trade names such as "Uvinul®" (Antara), "Cyasorb" (Cyanamid), "Tinuvin" (Geigy), and "Salol" (Dow). At present the most widely used stabilizers in the cosmetic industry are the benzophenones because a much greater variety of these is available. Compounds with different degrees of absorption, solubility and compatibility are commercially available, and an absorber to fit a specific application can be chosen. In the future we can expect a greater variety of benzotriazoles and substituted acrylonitriles, which will enable the cosmetic chemist to have an even greater choice in selecting an absorber to fit a particular application.

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HISTORICAL DOCUMENTS

DR. FRANK J. STEELE has been appointed by Society President Lester I. Conrad to write a history of the cosmetic industry of the 20th century. Only recently, Dr. E. G. McDonough pointed out that "the cosmetic industry of today is almost entirely a 20th century phenomenon. Most rapid development of our industry has taken place since World War I. Unfortunately, the scientific history behind this period of great expansion has not been recorded, and many of the men who have played a prominent role in developing our science and the products on which our industry is based are reaching a point in life where their historical insight may not be available much longer."

Dr. Steele, who is Chairman of the Library Committee of the SOCIETY OF COSMETIC CHEMISTS, has undertaken a program of writing a history of the cosmetic industry of the 20th century. Anyone who has pictures, records, biographies or other material which could be used for background material for this historical document is requested to communicate with Dr. Steele at 50 East Putnam Avenue, Greenwich, Conn. It is hoped that all members of the SOCIETY and all friends of the cosmetic industry will lend their support to this endeavor to insure the success of this history.

IS IT REALLY BAD?
A Proposal for the Toxicity-Testing of Drugs

By M. A. SCHNEIDERMAN*

Presented December 4, 1962, New York City

ABSTRACT

Clinical research differs from laboratory research in three major areas: size of the sample, variability in the experimental animal and possible experimental procedures. Within the limitations imposed by these differences, the clinician must strive to conduct a good ethical experiment. In the past, many ingenious attempts have been made to carry out acceptable experimentation. Most of the problems have not yet been solved, leaving the clinician still at loose ends about many of the things he would like to do. Some logically tight systems are available to him, and through very carefully pre-planned trials he may sometimes be able to answer the question, "Is it really bad?" A few of these systems are described.

THE REPORTS during the spring and summer of 1962 concerning thalidomide and the recent headlines about Preludin (1–3) and other drugs have made us more toxicity conscious than ever before. The charges and counter charges have led the statisticians to examine their ability to plan experiments that will yield adequate safety information. We do not come out too well, but here is what I see available to us, now.

Sometimes the newspaper accounts I saw reported things that looked like nonsense, or nearly nonsense. There were remarks like, "It has not been proved that Drug X caused the illnesses ascribed to it" or "It has been proved that Drug Y is thoroughly safe" or "There is no evidence that Drug P is responsible for deformities." These are nonsense for several reasons. First, I think we can agree that "proof" outside of deductive mathematics is almost impossible of achievement. Honest men can, and do, disagree as to what has been "proved." Second, these are not problems of "proof" with which we are faced. These are problems of decision and action. To talk of proof here is to drag red herrings across the trail. To talk of "responsibility" seems to me to be using language to cloud the issue. *The New England Journal of Medicine* speaks of the "benign hesitancy" of vitally interested parties "to accept any causal relation (4)."

New materials for entering the market can be looked at from the opposite poles. They can be considered safe until evidence accumulates to show

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that they are unsafe (innocent until proven guilty). Or, they can be considered unsafe until evidence accumulates that they are innocuous (guilty until proven innocent). Neither of these approaches is wholly sensible, because both neglect important elements. The first approach might represent the inherent bias of the drug producer. The second is contained in the sound advice from the American Medical Association that pregnant women take only "essential" drugs during the first trimester of pregnancy. It is also rather well summed up in these remarks of Blackader (5):

> "[Speaking of the many new drugs] a few may have some slight value; the majority, unfortunately, have little or none, and some appear to be distinctly harmful. Of the exact action of these drugs for good or evil we have at present little knowledge, except the statements, which are invariably much prejudiced, of the commercial houses introducing them.
>
> "Many of these so-called new drugs, introduced even by reputable houses, have been shown by analysis to be merely a mixture of old and well-known drugs.... It appears to me, therefore, to be of the utmost importance that physicians should accept all unproved statements very cautiously and should still rely almost entirely on the standard official preparations of which the exact composition and physiological action is well known."

This was not testimony given before the Kefauver Committee. It was not argument given to support a more vigorous Food and Drug Administration. It was contained in a paper published fifty years ago, in the *Canadian Medical Association Journal.*

Why is neither of these approaches satisfactory? Something is being neglected. This something is the value judgment that must be made and weighed. What are the gains to be achieved—at what cost? Sometimes the issue is clear. Suppression of morning sickness is a minor gain. (I say this as an unbiased, never-pregnant male.) Phocomelia, even in a few cases, is a dreadful cost. The issue of whether it has been *proved* that thalidomide causes or is *responsible* for phocomelia is not the dominant element here. The high cost associated with a high probability associated with a small gain are enough to decide actions—whether an air-tight case has been made or not. In the Preludin problem we have a similar high cost, and small gain, but this time these are tied together by what today looks like a low probability. It is no wonder that people do not agree on what to do with this one.

Aside from being eligible for membership in the American Medical Association, how else does the physician differ from laboratory scientists? Primarily, in his daily practice he has to make decisions and take action in the face of (what he knows to be) incomplete evidence. We do not. We can delay. We can hesitate. We can back-track. We can go back to the laboratory to get more data. Most of the time he cannot. Fortunately,

people and illnesses being what they are, his incomplete evidence decisions usually turn out satisfactorily. The patient gets well and lives. Have this happen sufficiently often, and a man begins to get the feeling that he can intuit pretty well (and some can), and soon he may be willing to make decisions, to reach conclusions with incomplete evidence even when he does not have to and when he would be wiser not to. This becomes an occupational illness and it should be treated as such—with care and kindness and not contempt. The physicians need help here, not snide remarks.

In addition, the physician has several other problems that we can skirt. His laboratory animal is man, and as the *British Medical Journal* recently wrote in a leader (6), quoting Bernard, "The principle of medical morality consists, then, in never performing on man an experiment which could be harmful to him in any degree whatsoever though the results may be of great interest to science—that is, of benefit to save the health of others." Since we lab types are anthropomorphic people and conceive of a God created in our own image, we are not restricted from experiments on mice, rabbits, guinea pigs, dogs, monkeys, etc., which could be harmful to them. The physician is limited.

This limitation means that he must never test a new drug unless he is honestly and firmly convinced that it is at least as good on balance as the best existing drug. And he must come to a conclusion with a minimum experiment size. Under the Bernard proscription he certainly cannot test on man solely for toxicity. The problem raised earlier about the potential gains and losses, benefits and costs arises here again. Formal statistical decision theory, which is a common technique in "cost" problems, is extremely difficult and perhaps impossible to apply here. Here we do not have a purely self-contained system. There are gains (or potential gains) to more than one party. There are losses or potential losses to more than one party. I do not know how one would balance the financial gains of a drug house against the physical, emotional and financial costs to a family with a deformed child. This is crudely put in the hope that it will make clear that the decision theoretic solution when the formulas are set down from the drug makers' point of view may be different from the decision theoretic solution arrived at by starting from the drug takers' point of view.

In reporting the paper that appeared in the November 17, 1962, issue of the *British Medical Journal* which said . . . "that two women who had taken Preludin gave birth to deformed babies," the *New York Times* (1) also reported that "Physicians said that it could have been a coincidence." And certainly it could have. How would one know? How would one go about finding out?

Figure 1 relates to this problem. It shows the results of computations (7) to find the sample sizes necessary to show an increased incidence of thyroid cancer. This is a rare disease, so the example may be extreme.

Incidence is about 5/100,000 per year in the United States. To show a 50% increase (with 95% certainty that if so large an increase did occur the observer would correctly call it "significant" at the P $\leq$0.05 level) one would need over 10^6 man-years of observation. For a hundred-fold increase, 10,000 % of the base, one would need (under the same limitations) over 1000 man years of observation.

Notice that even with so large a body of observation one does not have "proof." The differences found could still have been due to "coincidence." Yet this is what it would take to produce evidence that meets current standards of the laboratory worker. Is it any wonder that the physician would like to work with less?

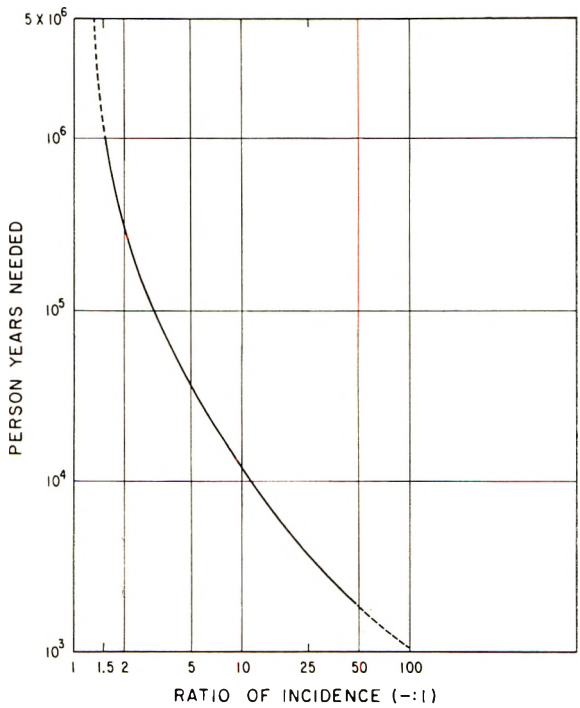

Figure 1.—Sample sizes needed to show increased incidence of a rare disease (5/100,000) with 95% assurance that an experiment will show a significant difference at the P $\leq$ .05 level.

One last remark on Fig. 1. To disclose "any difference, however small" would require an infinite sized population—or in the absence of so large a group, an experiment comprising all the people on earth.

This means (to me, at least) that absolute safety cannot be guaranteed. What then can be achieved? Any material given at high enough dose levels will produce toxicity. If some ingenious experimenter can produce

toxicity in his experimental animals at some outrageous dose level, does this imply that the drug is not useable, at all?

I would like to give the suggestions, with some minor modifications, of a colleague (8). Consider the idea of "virtual safety." That is, if you could find a dose level which would produce a defined toxic response in say 1 in 100,000,000 would you accept this as "virtual safety?" I do not particularly like a fixed level, because I think costs must be related to the illness or condition for which the drug is to be used. "Virtual safety" for an anticancer drug may be at the level of 1 in 100 (or higher, perhaps). "Virtual safety" for a decorative cosmetic may have to be set at less than 1×10^{-8}.

However, if we can agree that a concept such as "virtual safety" is acceptable, recognizing that it may be operationally different for every different material examined, we may be on the way to a realistic experimental determination of a "safe" dose. The determination of "virtual safety" might have to come about as a result of a bargaining process between Carson (9) and Eckardt (10) or other such equally involved people. It is something that one would hope reasonable people working with each other could agree upon. Perhaps a third party might be necessary.

In general this is the procedure: Take the existing experimental data. Say that at some fixed dose, N_1 persons have been observed, and that n_1 have shown the toxic signs we are concerned with. Find the p_u (read as "p, upper") value of a proportion, p, which could experimentally have given n_1/N_1 as its lower 99% limit. (For example if $N_1 = 100$, $n_1 = 0$, then a little algebra shows $p_u = 0.045$.) From this value of p_u extrapolate downward a response curve with a suitably shallow slope. Mantel (8) suggests a linear dose response curve with a slope of one probit (one normal deviate per tenfold dilution). For this configuration the "virtually safe" dose (at a level of 1 per 100,000,000) is 1/8300 of the dose at which there were 0/100 toxic responses.

The larger the experiment (which shows n_1 = zero toxic responses) the higher the "virtually safe" dose will be. By a rather ingenious handling, Mantel also shows how data from several experiments can be combined and how results where there is some observed risk (including "natural" response) can also be used.

Here is a procedure that makes sense. It recognizes that guarantees of absolute safety are impossible. It makes no demands for "proof" where proof is impossible. It aims for goals that reasonable men can agree upon. It does require facing the real issue of costs *versus* gains, to set these goals. These are subjective, and they embody value judgments. We cannot escape them except in scientific sterility.

This leaves at least one more problem. What does one do when the "virtually safe" dose turns out to be much lower than any possible therapeutic dose? Here, I would join the American Medical Association (if they

would have me) and say, "Don't use it." Here we must be like Caesar who, when asked why he parted with his wife because of gossip about her behavior, replied, "I wished my wife to be not so much as suspected" (11).

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PARAMETERS OF EMULSION STABILITY*

By Robert D. Vold, Ph.D., and Robert C. Groot, Drs.†

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Abstract

In this report a clear distinction is made between the various usages of the term "stability," and consideration is given to the fundamental properties of the system which are likely to be important according to each definition. The ultracentrifugal method is then described briefly and its use illustrated for determining the effect of the concentration of sodium dodecyl sulfate and of added sodium chloride on the ultracentrifugal stability of Nujol-water emulsions. Possible chemical changes are not considered in this presentation, and the emulsions treated are all of the oil-in-water type, although many of the same considerations would apply to water-in-oil emulsions.

Introduction

There is a continuing need for a reliable, rapid method for the prediction of emulsion stability and for a better understanding of those factors which are of greatest importance in affecting the stability. This has led to a resurgence of interest in centrifugal methods as a possible tool for the rapid characterization of emulsions (1–5). However, many empirical correlations of the results of such experiments with long term observations of the emulsions under shelf conditions will be required before it can be established whether the results of the accelerated ultracentrifugal experiments can be used to predict the stability under ordinary conditions. Nevertheless, the ultracentrifugal method affords a convenient method for identification of the important variables involved and for describing them in terms of an objective quantitative measure.

Kinds of Stability and the Factors Influencing Each

Shelf Life

In common usage stability is often equated with long shelf life, i.e., little or no change in properties or appearance on undisturbed standing

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under natural conditions for long periods of time. It is certainly a worthwhile endeavor to attempt empirical correlation of various laboratory tests with such observations since this may be the only definition of stability having commercial validity. But one must resist the temptation to generalize and remember that what holds for one type of system may not hold for another.

Creaming or Clearing

Creaming, or clearing, is a separation into layers of concentrated emulsion and dispersion medium, resulting from upward sedimentation of the drops of dispersed phase. Consequently, its rate will be strongly influenced by the viscosity of the medium, the density difference between the phases, and shear gradients resulting from either thermal or mechanical convection. While an emulsion showing such separation into layers might well be classified as unstable in terms of a shelf life criterion, it is not genuinely unstable in a colloid chemical sense since the oil phase remains dispersed as drops even though these may be concentrated or flocculated. Generally the creamed emulsion can be restored to its initial state by simple inversion.

Simultaneously with sedimentation there may also be a flocculation process occurring, aggregation of two or more drops to form a single kinetic unit but with each drop maintaining its individuality. Since single drops and aggregates will sediment at different rates according to Stoke's law, the rate of this flocculation process becomes important in any study of creaming.

The flocculation rate can be rationalized in terms of the repulsive forces tending to keep the drops apart and the attractive forces tending to bring them into contact. Among the former are electrostatic repulsion, which is governed by preferential adsorption of ions at the interface, and the ionic strength in the solution between the drops. Large drops, or aggregates of smaller drops, may also be broken up by shear gradients. In the case of water-in-oil emulsions steric hindrance of the adsorbed chains of emulsifier molecules can result in an entropic repulsion effective only at small distances of separation (6, 7).

Van der Waals attraction constitutes a general cause of flocculation of suspensions and emulsions and is likely to be important up to distances of separation of the order of the drop diameters. Its magnitude is determined largely by the polarizability and may also be strongly influenced by the nature of the adsorbed layer surrounding the drop (8). If the drops are sufficiently small, Brownian motion may tend to bring them into contact, but for larger drops this effect will be minor; only the convection currents due either to thermal gradients or mechanical agitation will be important.

Coalescence or Breaking

Coalescence, by which is meant irreversible formation of larger oil drops or of a separated bulk oil phase, represents the ultimate destruction of the emulsion. When a colloid chemist speaks of emulsion stability it is resistance to this process which he has (or should have) in mind. The rate-determining step in this process might be the rate at which water can drain from between the flocculated oil drops, the rupture of the adsorbed film of stabilizer surrounding the drops, the rate at which desorbed emulsifier can diffuse away from the interface where coalescence is occurring, or the effect of electrostatic attractions and repulsions on the rate at which drops come into actual contact. Much of the current theoretical research on emulsions is directed toward trying to differentiate among these alternative possibilities.

The hydrodynamic problems involved in the rate of approach of drops toward a plane interface or toward each other have been studied extensively by Mason (9, 10) and are also involved in the studies of the rate of thinning of soap films by Mysels and Overbeek (11, 12). The equations derived suggest that, as the radius of the drops becomes smaller, the rate of approach under a given driving force should become greater, i.e., the water between the drops should be squeezed out more rapidly, thus causing them to come in contact sooner.

Alternatively, the slow step in the process may be the rate at which the adsorbed stabilizer surrounding the drops is displaced, enabling coalescence to occur. This will depend primarily on the mechanical properties—surface viscosity and surface yield value—of the interfacial film. Since rupture of the film involves an initial increase in area, it may be that a higher interfacial tension may be desirable for stability even though this might make initial emulsification difficult.

The role of zeta potential, with its effect on electrostatic interactions, is still somewhat controversial with respect to the coalescence process. While it is necessarily important in a consideration of flocculation, it may well be that it has only a minor effect on the rate of coalescence.

Interpretation of these mechanisms in terms of molecular explanations is of both great theoretical interest and distinct practical importance with respect to suggesting possible ways of increasing or decreasing the stability of a given system. Orientation of molecules in adsorbed films, closeness of molecular packing, the cohesive forces between the molecules in the film, and electrostatic repulsions between the charged head groups of the adsorbed molecules will have an effect not only on surface viscosity and surface yield value but also on the electrical interactions. The magnitude of the repulsive force, calculable from the theory of the electrical double layer, will be greatly affected by the addition of indifferent electrolytes, or even by

increasing the concentration of an ionizable stabilizing agent. Since most emulsifying agents are association colloids, it becomes important to determine whether it is the monomer or the micelle that is effective in stabilization and to recognize in the case of colloidal electrolytes that the critical micelle concentration (cmc) sets an upper limit to the attainable concentration of monomer ion. Moreover, this limiting value is greatly decreased by addition of simple salts which lower the cmc.

Changes in the volume ratio of oil to water may well modify the relative importance of the preceding variables.

Methods for the Measurement of Stability

What is most needed for further progress in the field of emulsion technology is development of a sufficiently detailed theory of stability which could give a mathematical prediction of a rate or an equilibrium quantity, together with an experimental method which truly measures the quantity which is predicted. None of the currently available methods is genuinely satisfactory (5). Change of total interfacial area with time is generally insufficiently sensitive. Determination of the change of drop-size distribution with time is a very tedious experiment, although the recent introduction of the Coulter counter greatly increases its feasibility. Moreover, different systems appear to behave differently, since in some the size distribution changes reproducibly (13) while in other cases (5) there is little or no change with time. In any event, the ultimate criterion of instability is the appearance of free oil, and there is no clear proof that this is greatly dependent on the drop size distribution within the emulsion. Centrifugal methods for direct measurement of the rate of separation of free oil are generally too slow with all except relatively mobile liquids, and with the latter are frequently beset with difficulties, due to deformation of the liquid-liquid boundary on stopping the centrifuge. Rheological methods may be of considerable empirical value but are of limited use in understanding the nature of the processes occurring, because of the dependence of the rheological properties on a large number of other factors in addition to the stability of the emulsion.

Use of the ultracentrifuge for evaluation of stability has the advantage that the rate of appearance of demulsified oil is measured directly rather than some other property which it is hoped will be proportional to it. It results in a quantitative characterization of a stability attribute of the emulsion within a precision of 3 to 5%. Finally, it offers the advantage of speed, since it is possible to complete the preparation, measurements and calculations within two days.

There are, however, some serious disadvantages as well. It is not certain that it can be used effectively with very viscous systems or very stable emulsions. The equipment involved is relatively expensive and the tech-

nique exacting. The nature of the rate-determining step in the process is not yet established, whether it be rate of coalescence of drops, with the larger ones then moving upward, the rate of coalescence of the drops with the bulk oil phase, or the rate of transport of the drops through the creamed emulsion—the last certainly not describable in terms of Stoke's law.

Most serious, however, is the difference in physical state between the "emulsion" present in the ultracentrifugal field and the original emulsion as it would exist in a container after preparation. In the ultracentrifuge the flocculated emulsion contains only trace quantities of water, which shows that the original spherical drops have been deformed to a space-filling shape. This may account for the relative insensitivity of the rate of separation of free oil—here defined as the ultracentrifugal stability—to the size distribution of the drops. Despite the absence of measurable quantities, some water does remain in thin lamellae in the flocculated emulsion in the ultracentrifuge so preserving the identity of the dispersed oil "drops," as shown by the opacity of the system, its coloration in the presence of Orange II, and its ease of redispersion to give an emulsion containing a proportion of fine drops of the same size as those in the original emulsion (2).

This difference in state, however, implies that the results of ultracentrifugal analysis cannot be used directly to predict the behavior of a natural emulsion where both flocculation and coalescence properties may be important. Before use in this fashion it will be necessary to carry out careful shelf tests of considerable duration in order to establish some empirical correlations. But the ultracentrifugal method can yield a quantitative measure of the effect of changes in operating variables such as the method of emulsification, the concentration of the emulsifier, the effect of addition of electrolytes, etc., and so help to identify what the rate-determining processes are from a fundamental point of view. This understanding can then be applied qualitatively and semi-intuitively to the still more complicated practical situations.

Ultracentrifugal Technique

The method of using the ultracentrifuge to study the rate of separation of oil from oil-in-water emulsions has already been described (4, 5). In order that results on different emulsions should be truly comparable, the equilibrium concentration of emulsifier in the aqueous phase must be the same after emulsification of the oil and water. This necessitates preparation of emulsions having the same drop size distribution, since otherwise differences in adsorption due to the differing interfacial areas will result in different final states even though the initial compositions were the same. This is possible only if the initial emulsion is always prepared using the same mechanical homogenization of the same volumes of oil and water and a constant concentration of emulsifier. In our work 150 ml. of Nujol was

first stirred with 120 ml. of 0.2% sodium dodecyl sulfate (SDS) (solvent-extracted and salt-free) for five minutes at 5000 r.p.m. with a Brookfield Counter-rotating Mixer, followed by four passes through a Cenco hand homogenizer. After standing twenty hours, 45 ml. portions were withdrawn and 5 ml. of 0.2% SDS in water or in salt solution were blended in by gentle inversion to give a series of emulsions, all of 50% Nujol-50% water phase volume ratio and the same drop size distribution and SDS concentration but containing varying amounts of salt.

The similarity of the drop size distribution (mean diameter about 3μ) was evaluated in terms of the specific interfacial area of the emulsion, since the total oil-water interface is larger the smaller the drops. Areas were determined from the slope of the Langmuir equation fitting the results for adsorption of SDS at the interface, and an assumed value of 50 Å^2 for the area of an adsorbed molecule at the interface.* The amount of SDS adsorbed was determined from its known initial concentration in the aqueous phase and the analytically determined equilibrium concentration in a portion of the aqueous phase separated by low speed (5000 r.p.m.) centrifugation. Emulsions for this purpose, and for studying the effect of SDS concentration on the stability, were prepared by blending in 5 ml. of more concentrated SDS solution with 45 ml. of the stock, prepared as described above, to give 50–50 oil-water emulsions with 0.2, 0.3, 0.35, 0.4, 0.45, 0.5 and 0.6% initial concentration of SDS in the aqueous phase.

Upon centrifugation in a Beckman Spinco Model E ultracentrifuge at 39,460 r.p.m. the 0.8 ml. sample of emulsion separates into transparent layers of oil and water, separated by a layer of opaque concentrated emulsion. The change of position of these boundaries on photographs taken at successive time intervals permits calculation of the rate of separation of oil from the emulsion. On samples with low concentrations (0.2%) of SDS about 20% of the oil was separated rapidly in the first fifteen minutes in the ultracentrifuge, after which the rate of separation of oil became constant for a long period, only beginning to decrease after about 60% of all the oil in the system had separated. It is the slope of the linear portion of the curve of per cent oil separated *vs.* time which is a reproducible characteristic of the emulsion and which is referred to as the ultracentrifugal stability.

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* The value of 50Å^2 for the area of an adsorbed SDS molecule at the oil-water interface is based on application of the Gibbs equation to interfacial tension-concentration curves as discussed by E. G. Cockbain, *Trans. Faraday Soc.*, **50,** 874 (1954); F. van Voorst Vader, *Ibid.*, **56,** 1067 (1960); W. Kling and H. Lange, *Proc. Second Intl. Congress Surface Activity*, Butterworths Scientific Publications, London, (1957), p. 295; A. S. C. Lawrence and O. S. Mills, *Ibid.*, p. 200. Individual values range all the way from about 30 to 80Å^2 depending on the concentrations of surfactant and of added electrolyte. Since all the numerical values reported in the present paper would be affected similarly by any change in the value used for this molecular area, none of the conclusions reached would be altered if this area were revised in the future.

Effect of Concentraton of Emulsifier or Salt on the Ultracentrifugal Stability of Nujol-Water-SDS-NaCl Emulsions

The utility of the ultracentrifugal method in investigating the effect of preparative variables on the stability of emulsions is well illustrated by the data obtained showing the changes resulting from alterations in the concentration of emulsifier or the addition of simple salts. In Fig. 1 the ultracentrifugal stability of 50% Nujol-50% water emulsions is plotted as a function of the equilibrium concentration of SDS in the aqueous phase of

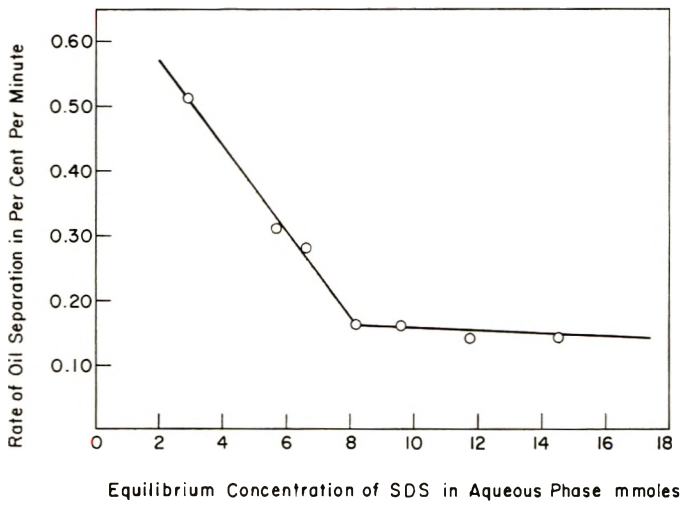

Figure 1.—Effect of concentration of sodium dodecylsulfate on the rate of separation of oil at 39,460 r.p.m. from 50% Nujol-50% water emulsions.

the emulsion. It is evident that the stability increases, i.e., the rate of separation of oil decreases, until the equilibrium concentration of SDS reaches about 0.008 moles/liter, after which the ultracentrifugal stability remains constant despite further increases in the concentration of SDS. It is extremely significant that this independence of concentration is reached just at the critical micelle concentration (cmc) of SDS (14), the value at which micelles form in the solution, with the result that thereafter the concentration of monomer ion remains nearly constant, all further additions of SDS simply increasing the number of micelles. Hence it appears that it is adsorption of the monomer ion of the emulsifier and not the colloidal component which is effective in reducing the rate of separation of oil.

Figure 2 shows that the rate of separation of oil from these emulsions varies exponentially with the concentration of sodium chloride present in the aqueous phase, as shown by the linear decrease with the logarithm of the salt concentration. Consequently the ultracentrifugal stability is very sensitive to the presence of salt, the rate of loss of oil being reduced to about

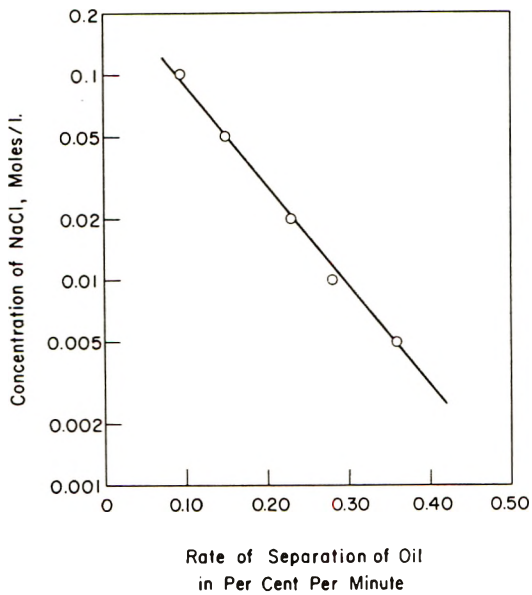

Figure 2.—Effect of sodium chloride on the rate of separation of oil at 39,460 r.p.m. from 50% Nujol-50% water-0.2% SDS emulsions.

$^2/_3$ of its initial value on making the aqueous phase 0.005 *M* in sodium chloride, as is seen from the data of Table III. In 0.1 *M* salt solution the rate of separation of oil is far less (0.095% per min.) than the slowest rate found with SDS alone (0.14% per min.; cf. Fig. 1). However, it should be borne in mind that about 6% of the oil in the salt-containing system separated in the first few minutes in the ultracentrifugal field, before the constant rate was established, whereas in the case of the salt-free, concentrated SDS emulsions virtually no oil was lost rapidly initially. These observations may be of considerable practical importance in accounting for variability in emulsion behavior resulting from use of different lots of emulsifier, since the latter may well contain variable amounts of electrolytes as impurities.

Molecular Explanations

Examination of the data in Fig. 1 and Table I shows that the rate of separation of oil reaches a limiting value of 0.14% per minute with increasing concentration of SDS, which is only about $^1/_3$ as fast as from an emulsion containing 0.2% SDS in the aqueous phase. It seems reasonable that attainment of this constant value should be related to saturation of the interface with adsorbed SDS. That this presumption is correct is indicated by the fact that the rate of oil separation decreases as the interface becomes more nearly saturated with SDS, and becomes constant

as soon as there is no further change in the fractional saturation (cf. Table I). It is also suggestive that the adsorption data conform quantitatively to a Langmuir equation, which predicts a limiting amount of adsorption determined by the quantity which can be present on completion of a close-packed monolayer.

Table I—Effect of Concentration of SDS on the Ultracentrifugal Stability at 39,460 r.p.m. of 50% Nujol-50% Water Emulsions, and on the Saturation of the Interface with Adsorbed SDS*

Initial Conc. of SDS in the Aqueous Phase, %	Rate of Oil Sepn., %/min.	Equilibrium Conc. of SDS— Moles × 10^3/l. in aq. Phase	Moles × 10^6 Adsorbed per ml. Oil	Fraction of Langmuir Saturation Adsorption
0.2	0.51	2.89	4.08	0.65
0.3	0.31	5.66	4.76	0.75
0.35	0.28	6.59	5.57	0.86
0.4	0.16	8.15	5.74	0.91
0.45	0.16	9.66	5.97	0.93
0.5	0.14	11.76	5.61	0.89
0.6	0.14	...	...	...

* The values reported here are the average of data obtained on emulsions with specific interfacial areas of 1.85 to 1.92 × 10^4 cm.^{2}/ml. oil as determined from adsorption data.

There are, however, certain difficulties with this explanation. Since adsorption of ions is occurring at a charged interface, there should be an electrical work term in the adsorption equation (15) which would invalidate the simple Langmuir equation and result in changes in adsorption due to changes in the ionic strength of the solution. Moreover, a change in the slope of the line obtained on plotting the adsorption data according to the linear form of the Langmuir equation might have been anticipated at the cmc, and none was found. There is also a little uncertainty with respect to the total area of oil-water interface available for adsorption during ultracentrifugation, since the drop shape is no longer spherical under these conditions. Finally, the limiting adsorption achieved is less than the saturation limit (90% in the emulsions of Table I; 86% in the emulsions of Table II) calculated from the Langmuir equation fitting the data. This, in turn, may be caused by changes in the area per adsorbed molecule resulting from added salt, or even from increasing concentration of the ionogenic emulsifier itself.

The marked increase in ultracentrifugal stability resulting from increasing the concentration of SDS or adding sodium chloride might be related to increasing the number of SDS molecules packed in the interface, or to increase in the surface viscosity or development of a surface yield value. That it is not merely the latter is suggested by the fact that with a 50% Nujol-50% water-0.2% SDS emulsion with a rate of separation of oil of 0.47% per minute at 39,460 r.p.m., additions of 1% and 5% lauryl alcohol on the basis of the aqueous phase only decreased the rate

to 0.42 and 0.43%, respectively, even though lauryl alcohol is known to rigidify films of adsorbed SDS at the air-water interface (16). This is in marked contrast to the pronounced effect of addition of salt, where 0.1 *M* NaCl reduces the rate of separation of oil to less than $^1/_5$ of its initial value (cf. Table III).

TABLE II—EFFECT OF CONCENTRATION OF SDS ON COVERAGE OF THE INTERFACE WITH ADSORBED SDS IN 50% NUJOL–50% WATER EMULSIONS*

Initial Conc. of SDS in the Aqueous Phase, %	Fraction of Langmuir Saturation Adsorption	Area, Available† per Adsorbed SDS in Å²
0.20	0.64	78.8
0.30	0.74	66.9
0.35	0.80	62.9
0.40	0.86	58.7
0.45	0.85	58.9

* The values reported here are the average of data obtained on four or five emulsions with specific interfacial areas of 1.81 to 2.07 × 10^4 cm.²/ml. oil as determined from adsorption data.

† These values are obtained simply by dividing the specific interfacial area by the product of Avogadro's number and the experimentally determined moles adsorbed at the interface per ml. oil. They will all be changed by a constant factor if the value of 50 Å² per adsorbed SDS used in the calculation of specific interfacial area should ever be revised in the light of new data.

TABLE III—EFFECT OF SODIUM CHLORIDE ON THE ULTRACENTRIFUGAL STABILITY AT 39,460 R.P.M. AND ON THE INTERFACIAL ADSORPTION OF SDS IN 50% NUJOL–50% WATER–0.2% SDS EMULSIONS

Conc. of NaCl, Moles/Liter	Rate of* Oil Sepn., %/min.	Area Available† per Adsorbed SDS in Å²
0.0	0.51	78.9
0.005	0.36	71.0
0.01	0.28	68.8
0.02	0.23	...
0.03	...	63.1
0.05	0.15	60.6
0.1	0.095	57.4

* Data reported for the ultracentrifugal stability were obtained with three different emulsions. The specific interfacial area was only determined for one, the value being 1.81 × 10^4 cm.²/ml. oil. The others probably had comparable but not identical areas.

† The values reported here are the average of the data obtained on three emulsions with specific interfacial areas of 1.96, 1.94 and 1.81 × 10^4 cm.²/ml. oil as determined from adsorption data.

The best measure of the closeness of packing of the SDS molecules in the interfacial film in the case of emulsions of varying specific interfacial areas is the area available per adsorbed molecule. Table II shows that as the concentration of SDS is increased more is adsorbed so the area per molecule decreases, reaching a limiting value of about 59 Å². This seems to be a saturation limit and is reached when the concentration of SDS in the aqueous phase of the emulsion reaches the cmc. Simultaneously the rate of loss of oil becomes constant at 0.14% per minute despite further increases in the initial concentration of SDS.

It is clear from Table III that addition of salt greatly increases the adsorption of SDS, the area per molecule at the oil-water interface in 0.2% SDS emulsions with high concentrations of sodium chloride actually being less than the smallest values attainable with SDS alone even at high concentrations (cf. Table II). This may result from the effect of the added salt on reducing the zeta potential at the interface, thus reducing

the electrical work required to bring additional negatively charged dodecylsulfate ions into the negatively charged interface. In addition, the presence of sodium chloride results in closer association of the sodium ions with the dodecylsulfate groups in the interface, thus reducing the effective negative charge and permitting closer packing of the SDS residues in the film.

That molecular packing does not by itself constitute a complete explanation of the observations is shown by the fact that the actual number of SDS molecules per cm.^{2} of interface is not very different in emulsions containing 0.2% SDS, 0.1 *M* NaCl and those with 0.45% SDS, zero NaCl, the areas per molecule being respectively 57.4 Å^2 (Table III) and 58.9 Å^2 (Table II). Nevertheless, the salt-containing system separates oil only about $^2/_3$ as rapidly as the salt-free system, the two rates being respectively 0.095% per minute (Table III) and 0.16% per minute (Tables I and II). It would not be expected that this concentration of salt would have this large an effect on the rate of drainage of water from between the flocculated oil drops. Hence, it is tempting to assume that its chief effect is to increase the cohesiveness of the adsorbed stabilizing film by reducing the repulsion between the chains by shielding the charges on the dodecylsulfate groups. Consequently, the protective film surrounding the oil drops may not break as easily on contact, thus increasing the time required for coalescence to occur.

SUMMARY

Different usages of the term "stability," the means of measuring each, and the factors influencing each process leading to instability, are first discussed. In the case of the ultracentrifuge the quantity determined is the rate at which free oil is separated from an emulsion layer in which the drops are so deformed and so closely packed that very little water remains between them. Although not necessarily having a direct correlation with shelf life, such results are very useful in attempting to determine the nature of the rate-determining step in the coalescence process.

In conjunction with determination of interfacial adsorption, they are of particular value in quantitative evaluation of the effect of surfactant concentration, addition of salts, etc., on the rate of separation of oil. Thus it was shown that the ultracentrifugal stability increases with increasing concentration of sodium dodecylsulfate in the aqueous phase until the critical micelle concentration is reached, after which it becomes constant, independent of emulsifier concentration. Addition of sodium chloride was found to increase greatly the ultracentrifugal stability of the emulsions studied, the effect varying as the logarithm of the concentration of added salt. This result was shown to be related to an increase in the

adsorption of sodium dodecylsulfate in the presence of salt and a change in the characteristics of the adsorbed film.

(Received January 7, 1963)

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BOOK REVIEWS

STEROID DRUGS, by Norman Applezweig. McGraw-Hill Book Co., Inc., New York 36, N. Y. 1962. 742 pages, illustrated and indexed. Price $25.

The first three hundred odd pages of this work are as exciting to read as a "who dunnit" thriller. Author Applezweig, as one of the steroid pioneers, knows who started what and where. His description of the steroid cartel created by Schering Kahlbaum, Ciba and Organon (all of Europe); the pioneering work of Russell Marker for Parke Davis and Co., with whom he fell out; the development of Syntex in Mexico by Marker; the synthesis of cortisone by the Merck researchers; Searle's perfusion method of oxygenating steroids; the Upjohn fermentation process; the come lately companies like Pfizer, Glidden, General Mills, Protex, Diosynth; the replacement of Marker at Syntex by Rosenkranz when the former left; the work of Windaus, Wieland, Butenandt (student of Windaus) and Ruzicka as the four Nobelists, are only a part of the many thrilling episodes clarified and tied together by the author. Then there is (or was) the "patent pool" consisting of Research Corp., Ciba, Organon and Schering to whom Merck paid royalties on its synthesis of cortisone, the gradual invasion of this field by other companies; all this forms another fascinating facet of today's steroid picture. The author does not confine his remarks to U. S. companies. His adventure covers the international scene.

Further along are discussed the five main classes of therapeutic steroids: androgens, estrogens, progestins, glucosteroids and mineral corticosteroids. The cosmetic application of steroids (page 274) is reviewed in five pages of the text. The author makes a significant indictment of the cosmetic industry with his statement, "Much of the failure to make use of the opportunities for the use of steroids in cosmetics must be laid at the door of the cosmetic manufacturers, who, perhaps through discouragement or timidity, have not used the knowledge available from modern steroid research."

There are a few awkward sentences in this fascinating tale, as in the second paragraph on page 96. While insignificant, there is a discrepancy in the stated price of progesterone which "tumbled to $3.00 per gram. . . ." on page 12 while on page 24 the price tumbled "to less than $2.00 per gram. . . ."

The references are all very recent, reflecting the newness of the major steroid developments. Most of the bibliography dates between 1950 and the present time, but a great many references are dated from 1955 to 1960.

The section on steroids and cancer is well done (page 160). The development of antifertility agents from the progestins and the increasing usefulness of anabolic steroids are carefully documented. The section on the menstrual cycle is useful.

The many tables, some 400 pages in all, follow from page 312 to 731. The structural formulas of 1409

steroids are given in about 300 pages. The balance of the tables classify the biologically active steroids using the author's coding system.

Author Applezweig's work replaces nothing. But it does complement such texts as Fieser and Fieser's famous tome on steroid chemistry.—M. G. deNavarre, Beauty Counselors, Inc.

The Chemistry and Manufacture of Cosmetics, by Maison G. deNavarre. D. Van Nostrand Co., Inc., Princeton, N. J. 1962. Volume I, 389 pages; Volume II, 413 pages; both indexed and illustrated. Price $11.50 per volume. Volumes III and IV to follow.

The title retained from the original edition may disappoint. So far, the manufacture of cosmetics is emphasized to a lesser degree than in the first effort. At this point the indications are that the coverage will be complete, uniquely lucid and amazingly up-to-date, considering the fluid state of the legal background of the industry. The formulation ideas used in less conservative cosmetic environments are covered and should give this book broad international acceptance.

The working cosmetic chemist and his semitechnical associates will find a well of information. The understanding built up by the 35 years of the modern cosmetic industry is encapsulated by one of the industry's finest technical writers. Although of textbook quality, considerable astuteness in choosing collaborators has brought a freshness of readability to a work which will continue to be a standard reference for the cosmetic industry.

No errors in proofreading were noticed. The use of basic reference data throughout the body of the work makes for greater reading interest. The author has succeeded in dividing this complex technology in such a way that each volume is, in its own field, a complete reference book. At the published price of $11.50 per volume, they are within the reach of both established and aspiring cosmetic scientists.—W. B. Dennis, Chemway Corp.

The Professional Scientist: A Study of American Chemists, by A. L. Strauss and L. Rainwater. Aldine Publishing Company, Chicago 5, Ill. 1962. 282 pages, indexed. Price $6.00.

Strauss and Rainwater, with their collaborators, present a study of the American chemist as he views himself and, to some extent, as he is viewed by others. The study was undertaken by Social Research, Inc., at the request of Albert L. Elder, 1960 president of the American Chemical Society, and is an excellent sociological report on the status, expectations and characteristics of various divisions among chemists: research administrators, nonresearch administrators, Ph.D. researchers, non-Ph.D. researchers and bench chemists.

The authors discuss the meaning of the term "profession," the application of which is a matter of disagreement within several occupational groups, and examine the concern of chemists over their status as professionals. This concern is allied directly with attitudes toward physicians, who are generally believed to have greater prestige and higher income than chemists, as well as plans for training, accreditation and certification, unionization and other controversial topics.

The authors suggest that chemists must create a better public image of themselves. They indicate that the ACS, as the major scientific organization in the field, should take the lead in publicizing a professional image of the chemist in a manner

similar to the efforts of the AMA for the physician, a notably successful achievement.

The SOCIETY OF COSMETIC CHEMISTS comes in for special mention; one respondent is quoted to the effect that the SOCIETY is "of more practical help" than the ACS.

Another special mention is made of the fact that chemists, regardless of their problems with status, salary, advancement, etc., seem to be extraordinarily sure of themselves in their vocational choice. The authors note that "they are able to locate themselves fairly well [in their scientific and chemical world]—unlike many Americans who have trouble placing their own work in some meaningful frame." Furthermore, chemists are "incorrigible optimists" about the future of their field, in contrast to many other professionals; they feel that chemistry is an expanding field, with many opportunities—in fact, almost unlimited opportunities. Finally, chemists (along with physicists) are almost unique because there are no major splits between various specialities. This homogeneity suggests the possibility of cooperation for the betterment of the individual and of the profession, the latter being of almost equal importance with the former to most chemists.

This book is of value to those who are involved in guiding young people in a choice of careers, as well as to those who want an objective view of our culture. The individual chemist may be interested in comparing himself with other chemists and assessing some conceptions he may have about his occupation. Chemists who are curious about their fellow scientists and concerned about status and the public view of their profession will find this book interesting reading.—DR. AUDREY F. RIEGER

COMPREHENSIVE BIOCHEMISTRY, Volume II, by M. Florkin and E. H. Stotz. Elsevier Publishing Co., Amsterdam, New York. 1962. 328 pages, indexed. Price $14.50 singly, $11.50 in Series.

Florkin and Stotz have undertaken an ambitious task in editing this series of volumes which will make up "Comprehensive Biochemistry." Although the over-all plan is not fully established, it appears that this series may comprise as many as 20 volumes. The volume discussed here is Volume II of Section I, which is devoted to physico-chemical and organic aspects of biochemistry. Two-thirds of this volume are taken up by a chapter on the mechanisms of organic reactions by Bender and Breslow. Chapter II, Behaviour of Molecules in Solutions, and Chapter III, Diffusion and Osmosis, are contributed by W. D. Stein.

The chapter on mechanisms of organic reactions is devoted to a systematic description of the mechanisms of those reactions which may be of interest to biochemists. In view of the enormous latitude of biochemistry, it is fair to state that this chapter covers almost all reactions of interest to organic chemists. This chapter is not concerned with enzymatic reactions but is designed to bring "to . . . enzymology the fruits of organic chemistry." The discussion of mechanisms is descriptive, and the use of mathematics and of complicated kinetics is held to a minimum. As a result, this book should appeal to all those chemists whose mathematical background is a little shaky. Wherever kinetics are used to describe a series of reactions, the description is lucid and to the point. The discussion of the chemistry of the bimolecular elimination reactions can be recommended to anybody who wants to

refresh his knowledge of organic chemistry. Similarly, the discussions of the general acid and general base catalysis are worthy of careful study. The general treatment of the mechanisms of chemical reactions in this chapter is excellent, although many more up-to-date aspects have been neglected. Particularly striking by their absence are the recently elucidated mechanisms of reactions of disulphides which are of prime importance to biochemists and are believed to proceed *via* a homolytic mechanism (cf. Calvin's work on thioctic acid) or nucleophilic pathways (Fava, *et al.*).

The two chapters by Stein deserve special mention because they represent, in the opinion of the reviewer, a most readable description of the physical chemistry of solutions and the physical chemistry of diffusion in nonmathematical terms. The descriptive discussions of Raoult's law and of Hildebrand's regular solutions are excellent. Particular mention should be made of the chapter on diffusion in which diffusion is discussed not as a macroscopic but as a molecular or atomic process. The author describes the concepts of Danielli and presents a good introduction to the problems of cellular biochemistry.

Over-all, the volume is very readable and written in a very lucid style. In the reviewer's opinion, this volume could have been made more legible if the structural formulas were presented in larger type. Regardless of this minor defect, this volume makes good reading for most chemists who do not specialize in kinetics and physical chemistry.—M. M. RIEGER

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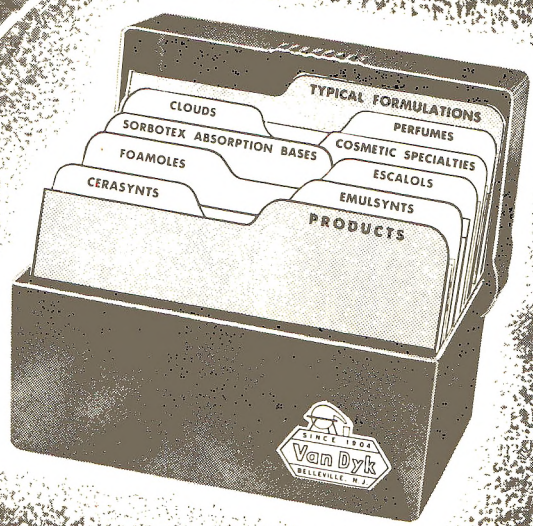

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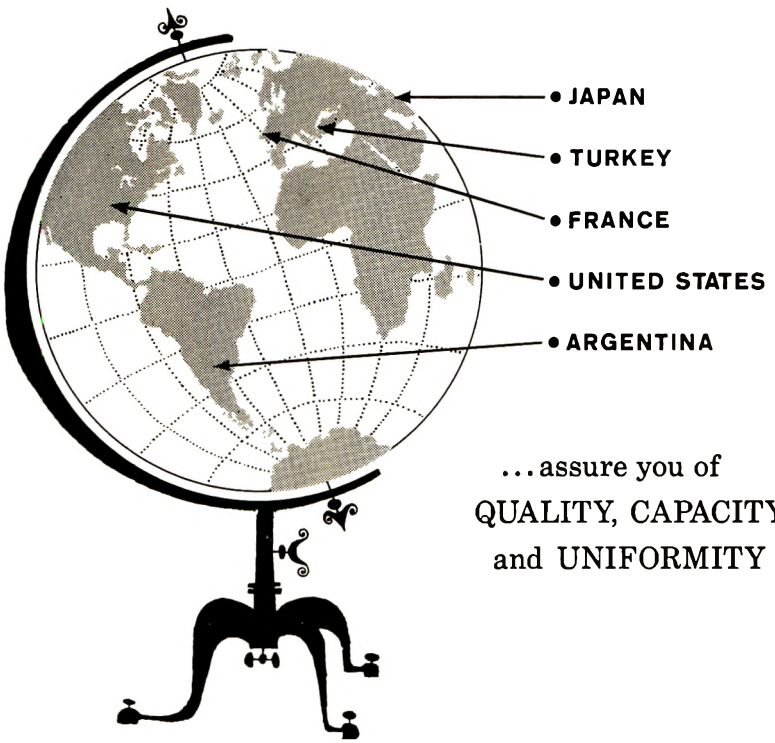

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