


Journal of the Society of Cosmetic Chemists

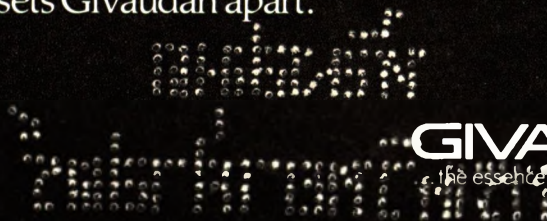
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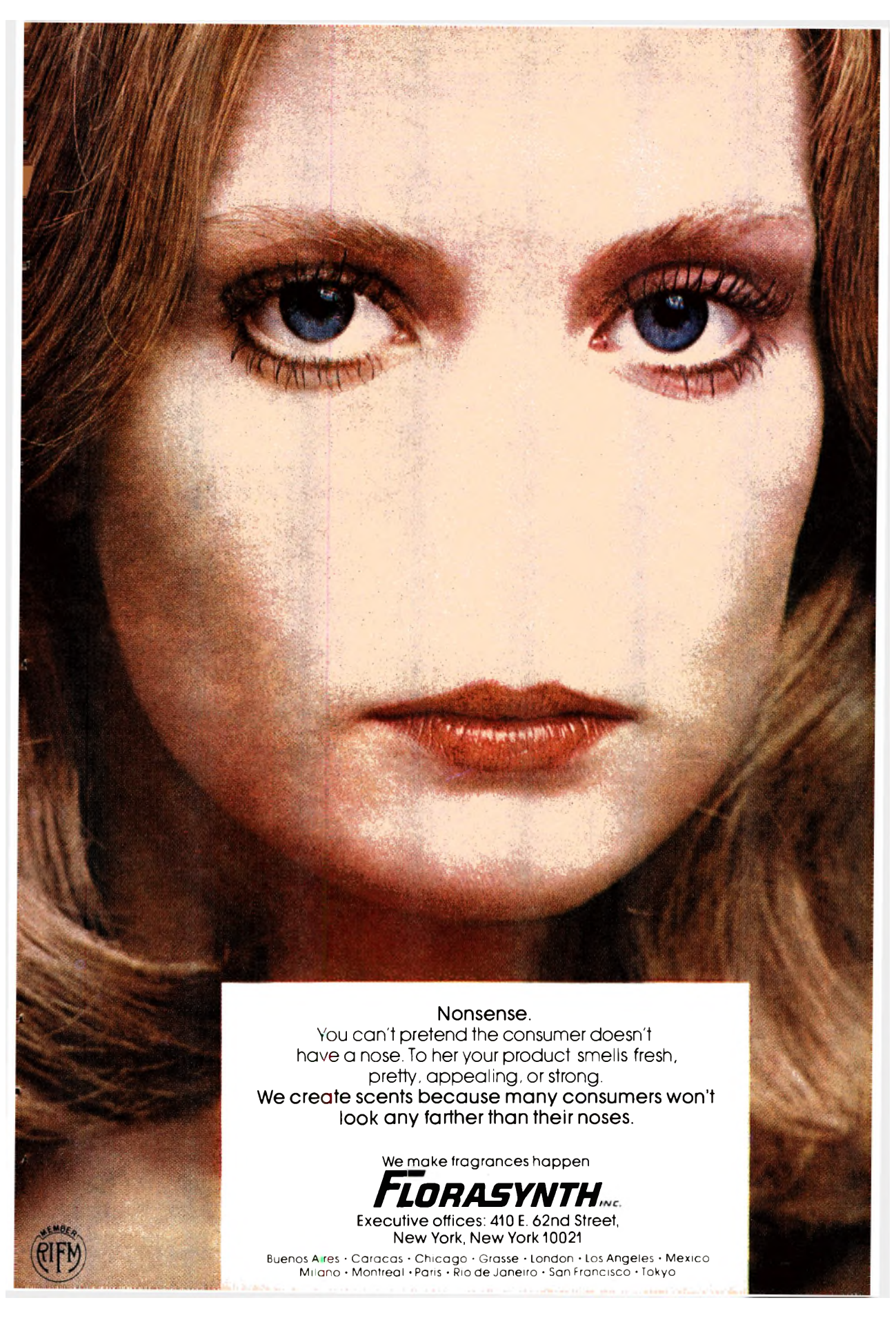
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SYNOPSIS FOR CARD INDEXES

The following synopses can be cut out and mounted on 3 x 5 in. index cards for reference, without mutilating the pages of the Journal.

An evaluation of dispersing agents in aerosol formulations. I: Synthetic esters: John J. Sciarra, Anthony Iannacone, and Lee Mores. *Journal of the Society of Cosmetic Chemists* 27, 209 (May 1976)

Synopsis—This study is concerned with determining the effect that various dispersing agents have upon the suspension and redispersibility of several solids commonly used in aerosol formulations. Talcum, starch, and aluminum chlorhydroxide were used with various dispersing agents (including isopropyl isostearate, propylene glycol dipelargonate, 2-ethylhexyl pelargonate, methyl myristate, propylene glycol monoisostearate, isopropyl myristate, and hexadecyl alcohol). The effect of these materials upon the different formulations was determined by a study of the rate of settling and redispersibility of the product. Further attention was given to the relationship between the overall usefulness of the dispersing agent in these formulations and its chemical structure. The solubility in several commonly used propellants of each of the fluids studied was also observed. In general, formulations containing the less polar dispersing agents settle rapidly, redisperse easily, and do not cake, while formulations containing the more polar compounds tend to behave in the opposite manner.

In order to determine the effect of particle size, as well as the effect of coating the solid particles with dispersing agent, formulations were prepared whereby the powders were dispersed in a mixture of propellant and dispersing agent. The results of this study were then compared to the results obtained by intimately mixing the insoluble powder and dispersing agent and then adding them to the propellant mixture. In general, similar results were obtained. These results were then correlated with the solubility of the dispersing agent in the propellant mixture.

Solubilization of essential oils with polyoxyethylene glyceryl fatty esters IV. The use of solvent couplers as auxiliaries in the preparation of pharmaceuticals: Karl Thoma and Günther Pfaff. *Journal of the Society of Cosmetic Chemists* 27, 221 (May 1976)

Synopsis—The utility of polyoxyethylene glyceryl fatty acid esters for the solubilization of essential oils was examined. The results with peppermint, lavender, anise, and clove oils are represented with the aid of phase diagrams. The surfactants' ability to solubilize these oils improves when the carbon chain of the fatty acids is shortened and when the polyoxyethylene chain length is increased.

Recoating of human hair by sebum: Hans Eberhardt. *Journal of the Society of Cosmetic Chemists* 27, 235 (May 1976)

Synopsis—The results of two model experiments show that sebum does not creep along the hair. Accordingly, the sebum which coats the hair does not originate from its follicle. It is assumed that the terminal hair picks up sebum mechanically from surrounding follicles.

The hair and the sebaceous gland together form the pilosebaceous apparatus in both man and hairy animals. The hair protects the body from loss of warmth, while the sebaceous glands protect the hair by covering it with lipid. Therefore, we can assume that the sebum, which is present in the hair follicle, is coating the whole hair. Greasing of the hair, which takes place during its growth out of the sebum-filled follicle, is of minor importance, since the rate of hair growth is only 0.35 mm a day. Moreover, recoating of hair by sebum occurs within a few days. Therefore, creeping of the sebum along the hair, as has been assumed by some authors (1), (2), seems to provide a natural explanation for the process of hair greasing.

An Evaluation of Dispersing Agents in Aerosol Formulations. I: Synthetic Esters

JOHN J. SCIARRA, Ph.D.,^{*} ANTHONY IANNACONE, M.S.,[†]
and LEE MORES, M.S.[‡]

Presented May 1, 1973, SCC Seminar, Cincinnati, Ohio

Synopsis: This study is concerned with determining the effect that various DISPERSING AGENTS have upon the suspension and redispersibility of several solids commonly used in AEROSOL FORMULATIONS. Talcum, starch, and aluminum chlorhydroxide were used with various dispersing agents (including isopropyl isostearate, propylene glycol dipelargonate, 2-ethylhexyl pelargonate, methyl myristate, propylene glycol monoisostearate, isopropyl myristate, and hexadecyl alcohol). The effect of these materials upon the different formulations was determined by a study of the rate of settling and redispersibility of the product. Further attention was given to the relationship between the overall usefulness of the dispersing agent in these formulations and its chemical structure. The solubility in several commonly used propellants of each of the fluids studied was also observed. In general, formulations containing the less polar dispersing agents settle rapidly, redisperse easily, and do not cake, while formulations containing the more polar compounds tend to behave in the opposite manner.

In order to determine the effect of particle size, as well as the effect of coating the solid particles with dispersing agent, formulations were prepared whereby the powders were dispersed in a mixture of propellant and dispersing agent. The results of this study were then compared to the results obtained by intimately mixing the insoluble powder and dispersing agent and then adding them to the propellant mixture. In general, similar results were obtained. These results were then correlated with the solubility of the dispersing agent in the propellant mixture.

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[†]St. John's University, College of Pharmacy and Allied Health Professions, Jamaica, New York.

[‡]Emery Industries, Inc., Fatty Acid Division, Cincinnati, Ohio.

INTRODUCTION

The dispersion and suspension of powdered solids in aerosols have presented many formulation problems. These problems have been mainly concerned with maintaining the solid in suspension, redispersibility of the solid, and the prevention of particle agglomeration and caking and valve clogging (1). Present day technology has overcome many of these problems through the use of suitable dispersing agents; careful selection of the solid; addition of other

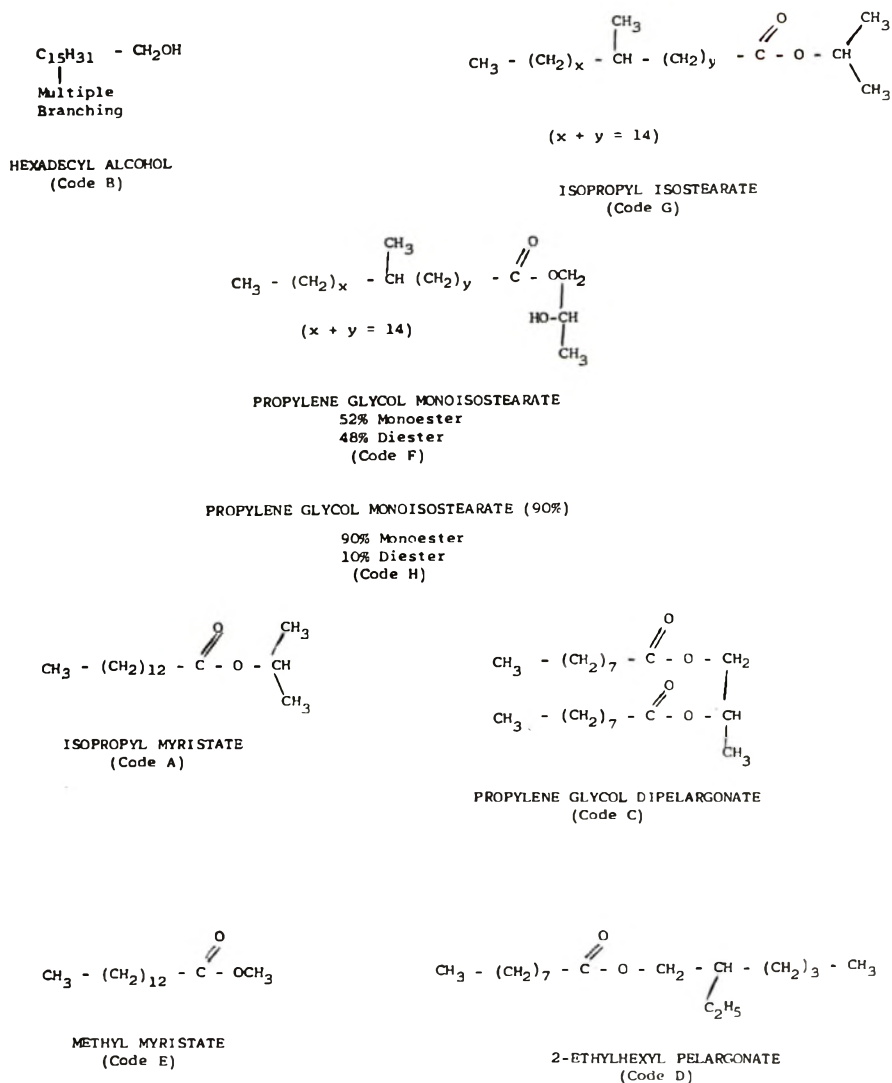


Figure 1. Chemical structure of dispersing agents

agents such as talc, starch, bentonite, and silica derivatives; and careful selection of suitable valves (2). With regard to this, another important aspect is that the particle size of the solid to be dispersed must be about $50\ \mu$ or less (able to pass through a number 325 mesh screen). A combination of many of these factors is used in order to formulate suitable aerosols, which contain dispersed solids (3,4).

In the past, various materials had been used as dispersing agents for these aerosols. They include isopropyl myristate, hexadecyl alcohol, mineral oil, and other similar substances. In addition, several surfactants, such as the sorbitan esters, have also been used as dispersing agents for these aerosols, although the use of these esters has been limited to those products containing very small quantities of powder such as is found in medicinal aerosols (5).

Preliminary studies, which employed several other materials, which are potentially useful as dispersing agents, revealed the possibility that the dispersing properties of the material may be related to the chemical structure of the compound. This observation has also been noted by others (6).

Several materials were selected for this study. They included isopropyl myristate, hexadecyl alcohol, methyl myristate, isopropyl isostearate, 2-ethylhexylpelargonate, propylene glycol dipelargonate, propylene glycol monoisostearate, and propylene glycol monoisostearate (90 per cent). The chemical structure of each of these materials is shown in Fig. 1. The effect of each of these materials upon the dispersion of aluminum chlorhydroxide complex, talc, and starch was determined.

The solubility of each of the above materials was also determined in various propellants and propellant blends so that the solubility of the substance in the propellant could be correlated with its suspending properties. Since viscosity changes were noted when the dispersing agent was mixed with the solid (in particular, combinations of aluminum chlorhydroxide complex with silica products), the viscosity of these systems was determined.

EXPERIMENTAL

Development of a Simple Method for the Screening of Dispersing Agents

This study was carried out to devise a simple technique for evaluating dispersing agents, which are useful with solids in aerosol formulations. Furthermore, it is desirable to effect this screening without the use of a pressurized aerosol system, thus allowing any laboratory without aerosol filling equipment to obtain a reasonable idea as to the potential performance of various products in an actual aerosol formulation. It was felt that if a system in which a nonpolar solvent, such as petroleum ether, was substituted for the propellant in a typical aerosol formulation, measurement of suspension and redispersibility properties of the solid material in this system would correlate to the same properties measured in an actual aerosol system. Several dispersing agents and

aluminum chlorhydrate (as the model solid), were evaluated at atmospheric pressure relative to their suspension and redispersibility properties in a nonpolar solvent system, which simulated the viscosity of a typical pressurized aerosol system.

A. Simulated Aerosol Formulation

Aluminum chlorhydrate ^o	5.0 per cent
Fumed silica [†]	0.1 per cent
Dispersing agent	4.9 per cent
Petroleum ether	90.0 per cent

B. Dispersing Agents

Isopropyl myristate
 Propylene glycol monoisostearate
 Isostearyl isostearate
 Isopropyl isostearate
 Propylene glycol dipelargonate

C. Preparation of Dispersion

The aluminum chlorhydrate, fumed silica, and dispersing agent were mixed together. A 6.0-g sample of this concentrate was then added to a 100-ml graduated cylinder, followed by addition of 54.0 g of petroleum ether. The cylinders were shaken by hand to give complete dispersion.

D. Measurement of Settling Rate and Ease of Redispersibility

The cylinders containing a homogenous dispersion of aluminum chlorhydrate and fumed silica were allowed to stand, and the volume of clear supernatant liquid was measured, starting with a 15-sec time lapse, until settling was completed. The final volume the solid occupied was also recorded. After 24 hours, the number of inversions required to redisperse the powder was measured. These results are shown in Table I.

Solubility of Dispersing Agent in Propellant

The approximate solubility of each of the dispersing agents studied was determined by adding a given weight of dispersing agent to an aerosol com-

^oChlorhydrol, Impalpable Solid, Micro-dry; Reheis Chemical Company, Berkeley Heights, N.J.

[†]Cab-O-Sil-M-5, Cabot Corporation, Boston, MA.

Table I
Settling Rate of Various Dispersing Agents in Petroleum Ether

Time Sec	Volume of Supernatant Liquid (ml)				
	Isopropyl Myristate	Propylene Glycol Monoisostearate ^a	Isostearyl Isostearate ^a	Isopropyl Isostearate	Propylene Glycol Dipelargonate
15	11	—	—	26	26
30	36	—	—	51	53
45	56	—	—	73	74
60	74	—	—	75	76
75	76	—	77	76	—
105	77	—	—	77	—
180	78	—	77	77	78
900	—	81	—	—	—
Final volume of solids (ml)	8	5	7	8.5	8.5
Number of inversions for redispersion	1	2	1	1	1

^aCould not measure prior to final settling due to cloudiness of supernatant liquid.

patibility tube. The tube was sealed using an aerosol valve, and the appropriate propellant or propellant blend was added by the pressure process (Propellant 11,^o 12,[†] and 114[‡] alone and blended were used). The tube was shaken and placed into a water bath at 25°C ± 1°. After 24 hours, the solubility was rated as either soluble (S), insoluble (IN), hazy (H), or slightly hazy (SH). Depending upon the observed result, another tube was prepared using more or less of the dispersing agent; more if the previous quantity had been rated soluble and less if it had been rated insoluble. In this manner, the approximate solubility was determined. The results are shown in Table II.

Suspension and Redispersion of Solids

The major objective of this portion of the study was to determine the effect that various dispersing agents have upon the suspension of the powder in an aerosol system. The evaluation was made on the basis of initial dispersibility of the powder, sedimentation rate of the dispersion, and redispersion of the solid after it stood 24 hours and then 1 week. The dispersing agent was added by two methods: by adding it to the liquid portion of the propellant and by dispersing the fluid onto the dry powder.

Three powders were dispersed in an aerosol system, which was comprised of mixtures of various dispersing agents, and Propellant 12/11 (50:50). The

^oTrichloromonofluoromethane.

[†]Dichlorodifluoromethane.

[‡]Dichlorotetrafluoroethane.

Table II
Solubility of Dispersing Agent in Propellants

Dispersing Agent	Propellant				
	11	12	114	12/11 (50:50)	12/114 (60:40)
Isopropyl isostearate	S (30) ^a	S (30)	S (30)	S (30)	S (30)
Propylene glycol dipelargonate	S (30)	SH (1)	SH (1)	S (30)	SH (1)
Propylene glycol monoisostearate	S (30)	S (30)	S (30)	S (30)	S (30)
Propylene glycol monoisostearate (90 per cent)	S (30)	S (30)	S (30)	S (30)	S (30)
2-Ethylhexylpelargonate	S (30)	S (30)	S (30)	S (30)	S (30)
Methyl myristate	S (30)	S (3)	S (3)	S (3)	S (3)

^aFigures in parentheses indicate per cent solubility; 30 per cent represents highest concentration studied; S stands for soluble; H stands for hazy solution or dispersion; IN stands for insoluble; and SH stands for slightly hazy.

powders included aluminum chlorhydrate, talcum^o and starch.[†] All powders passed through a number 325 mesh screen.

The powder/dispersing agent/propellant system was prepared in 100-ml aerosol compatibility tubes. The total volume in each tube was 80 ml. The formulations were shaken by inverting the tubes several times, and following complete dispersion, the tubes were placed in a ring stand, and the volume of supernatant liquid was measured.

Rate of Sedimentation—Four g of the powder was placed into a calibrated 100-ml aerosol compatibility tube. To this was added 35 ml of Propellant 11, followed by the addition of 4 g of the appropriate fluid. The tubes were sealed and Propellant 12 was added by the pressure fill method to bring the final volume to exactly 80 ml. The tubes were then placed into a water bath at 25° C ± 1° for at least 1 hour. Additional Propellant 12 was added when necessary, to bring the contents to final volume. The final mixture contained 5 per cent each of powder and dispersing agent. Each tube was shaken by inverting the tube several times to completely disperse the powder. The tube was then stored upright and the volume of supernatant liquid was measured over a 24-hour period. After 24 hours, the tubes were shaken and allowed to stand 1 week. The solids were then redispersed and the volume of supernatant liquid was again determined over a 24-hour period. These results are shown in Figs. 2, 3, and 4. No differences in the sedimentation rates were noted between the initial determination and the determinations which were carried out after 1 week.

^oItalian Talc # 1602; Whittaker, Clark & Daniels, Inc.

[†]Dry Flo Starch #78-1567; National Starch & Chemical Corporation.

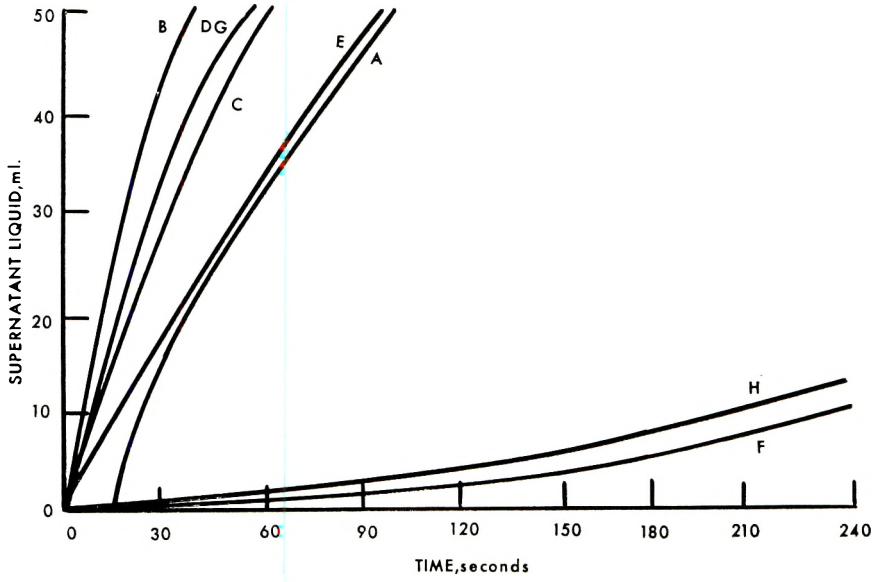


Figure 2. Aluminum chlorhydroxide complex with dispersing agent (for code see Fig. 1)

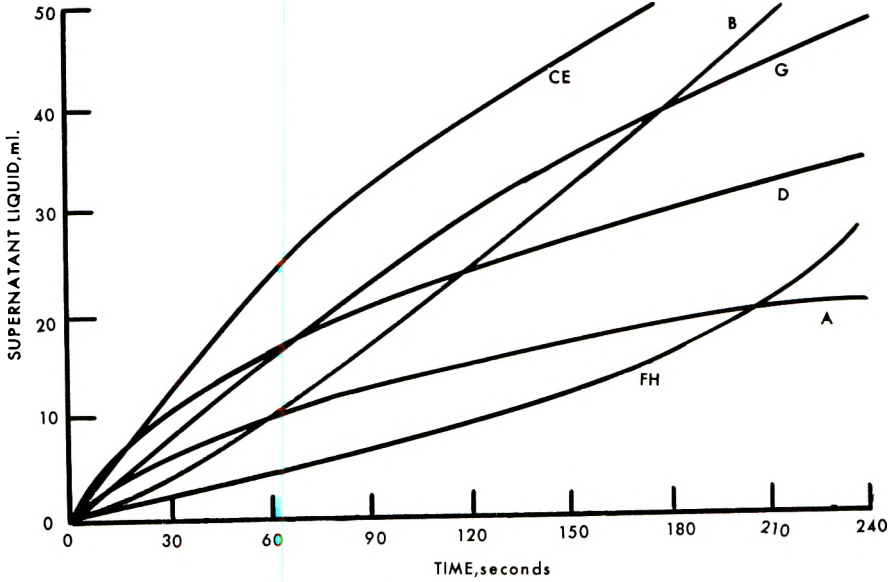


Figure 3. Starch with dispersing agent (for code see Fig. 1)

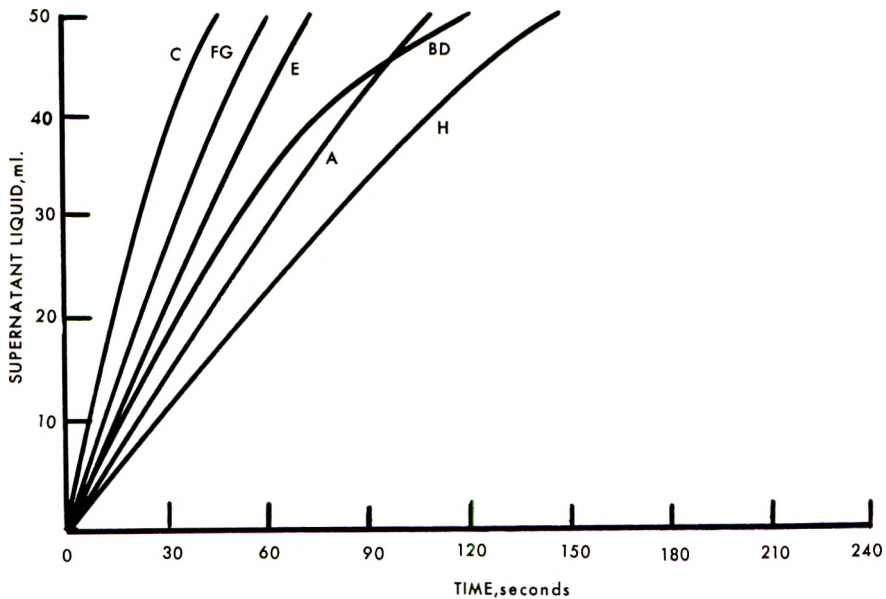


Figure 4. Talcum with dispersing agent (for code see Fig. 1)

Additional samples were prepared by placing 4 g each of the appropriate fluid and powder in a mortar. The mixture was thoroughly mixed and poured into a compatibility tube. Propellant 11 was used to rinse the mortar, and the rinsings were added to the compatibility tube. A total of 35 ml of Propellant 12 was added to bring the final volume to exactly 80 ml. The samples were placed into a water bath and treated as was previously indicated. Since no differences were noted between the results obtained when the dispersing agent was dissolved in the propellant or when they were dispersed directly onto the powder, the results shown in Figs. 2-4 are representative of the results obtained by both methods of mixing.

Dispersibility of Powders—Additional samples were prepared exactly as was previously indicated. After the contents of each compatibility tube had attained a temperature of $25^{\circ}\text{C} \pm 1^{\circ}$ and the volume had been brought to exactly 80 ml, the tubes were inverted several times to disperse the powder. The tubes were then stored upright, and the number of inversions required to fully disperse the powders after they had been standing 24 hours and then after they had been standing 1 week were recorded. Table III indicates the results that were obtained when the dispersing agents were added directly to the propellant, while Table IV gives the results when the dispersing agents were mixed directly with the solid.

Table III
Effect of Dispersing Agent/Propellant Mixture Upon the Redispersion of Solids^a

Dispersing Agent	Aluminum Chlorhydrate		Starch		Talcum	
	24 hours	1 week	24 hours	1 week	24 hours	1 week
Isopropyl myristate	5	5	2	2	5	5
Hexadecyl alcohol	4	4	2	2	6	6
Propylene glycol dipelargonate	3	3	2	2	3	3
2-ethylhexyl pelargonate	2	2	2	3	5	6
Methyl myristate	5	5	2	3	5	5
Propylene glycol monoisostearate	12	30	2	2	4	4
Isopropyl isostearate	3	3	2	2	5	6
Propylene glycol monoisostearate (90 per cent)	14	30	2	2	4	4

^aResults given as number of inversions required for complete redispersion of solid.

Table IV
Effect of Dispersing Agent/Solid Mixture Upon the Redispersion of Solids^a

Dispersing Agent	Aluminum Chlorhydrate		Starch		Talcum	
	24 hours	1 week	24 hours	1 week	24 hours	1 week
Isopropyl myristate	5	4	5	5	6	6
Hexadecyl alcohol	5	5	3	3	4	5
Propylene glycol dipelargonate	5	6	5	5	4	4
2-ethylhexyl pelargonate	2	2	6	6	7	8
Methyl myristate	2	3	12	15	4	4
Propylene glycol monoisostearate	18	30	15	15	4	5
Isopropyl isostearate	4	4	15	20	3	3
Propylene glycol monoisostearate (90 per cent)	20	30	15	20	7	7

^aResults given as number of inversions required for complete redispersion of solid.

Discussion of Results

The nonpressurized method, which was used to evaluate several dispersing agents proved to be successful. While petroleum ether was used in this study, other nonpolar solvents such as carbon tetrachloride and methylene chloride could also have been used. The measurement of the settling rate by this method showed four of the five materials to exhibit similar performances, with only the propylene glycol monoisostearate showing a significantly slower rate of settling. Isopropyl myristate showed a slightly faster rate of settling than the others.

With respect both to the final volume of the solid phase and the redispersibility, only the propylene glycol monoisostearate showed a significantly different performance. This sample was harder to redisperse and had a smaller final solids volume than the others tested.

The results obtained, when petroleum ether was used, compare favorably to the results obtained for these dispersing agents in similar tests, but in an actual pressurized aerosol system. The propylene glycol monoisostearate is the only agent studied with any functional group present other than an ester moiety. In this substance, the free hydroxyl group may slow the settling of the aluminum chlorhydrate as a result of its potential for hydrogen bonding. Once the aluminum chlorhydrate particles are coated, the hydrogen bonding may allow tighter packing and a stronger surface film as suggested by the observed smaller solids volume and increased difficulty in redispersibility. In general, the dispersing agents, which are more capable of strong intermolecular attractions allow a slower settling rate, but on the other hand, may cause redispersion to be more difficult.

The above results suggest that the method described here may be used as a preliminary screening test for potential dispersing agents for aerosol systems with respect to settling rate and redispersibility of aluminum chlorhydrate. More subtle evaluations must be carried out in an actual aerosol system in order to establish definitely the usefulness of the method.

It can be noted from Table II that isopropyl isostearate, propylene glycol monoisostearate, propylene glycol monoisostearate (90 per cent), and 2-ethylhexylpelargonate are soluble in all propellants studied. As can be predicted, Propellant 11 was the best solvent for most of the dispersing agents, while Propellant 114 was noted to be a poor solvent. This result was not unexpected because of the large number of fluorine atoms present in the Propellant 114 molecule. As can also be noted from Table II, the presence of Propellant 11 in a propellant blend will tend to increase the solubility of the dispersing agent in the other propellants.

Propylene glycol monoisostearate and the propylene glycol monoisostearate (90 per cent) consistently showed enhanced suspending properties when used with aluminum chlorhydrate, starch, and talcum. None of the materials used to suspend talcum were very effective. However, this effect is not surprising, since talcum has a fairly high density and is difficult to suspend. The fact that powders, which were suspended with propylene glycol monoisostearate as the dispersing agent, consistently showed a slower settling rate in aerosol systems, than did some of the other materials included in this study, confirms the results obtained when these mixtures were placed in the presence of petroleum ether in a nonaerosol system. Furthermore, this material showed complete solubility in the propellant systems. Isopropyl isostearate also showed a slower settling rate than did some of the other materials included in this study, although the differences were not as great as those noted with the

propylene glycol monoisostearates. It can also be noted that little, if any, difference existed with regard to the usefulness of the isopropyl isostearate or propylene glycol monoisostearates as suspending agents for the other materials studied.

It is also interesting to note, that when comparing the settling rate of the solids used in this study in the presence of various dispersing agents, propylene glycol dipleargonate was the least effective because the powders settled rapidly in the presence of this material. This material also showed the least solubility in the propellants. All of the samples showed a rather rapid rate of settling. In all cases, some settling occurred immediately with complete settling taking place in 4 to 5 min. Isopropyl myristate with aluminum chlorhydroxide did not show settling for the first 15 sec, as is shown in Fig. 2. Very little difference was noted between the reading taken at the 5 min and 24-hour time intervals. The results shown should be considered to be relative and of help in comparing the usefulness of the various dispersing agents studied, but not as absolute values.

Tables III and IV indicate the relative ease of redispersion of the solids using different esters. However, it is necessary to consider both rate of sedimentation and ease of redispersion when selecting a dispersing agent. It should be indicated that no anticaking agent, such as fumed silica was to be used in this part of the study. While the number of inversions required to effect redispersion would be different in the presence of an anticaking agent, it is believed that the relative order of usefulness of the esters would be the same.

SUMMARY and CONCLUSIONS

A study was made to determine the effectiveness of various dispersing agents, when they were used as suspending agents in the presence of aluminum chlorhydrate, starch, and talcum. The solubility of each of the dispersing agents in Propellants 11, 12, and 114 was also determined. A nonaerosol system, which was useful in screening various dispersing agents, was devised. Two methods of adding the dispersing agent to powder were studied and included addition of the dispersing agent directly to the propellant phase, as well as direct addition to the powder.

Of all the dispersing agents studied, propylene glycol monoisostearate (and the 90 per cent monoester) were found to be the most effective suspending agents for aluminum chlorhydrate, starch, and talcum. Very little difference was noted among the other dispersing agents used in this study.

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Solubilisation ätherischer Öle mit Polyäthylenglykolylycerin-fettsäureestern

4. Über die Anwendung von Lösungsvermittlern als Hilfsstoffe bei der Herstellung von Arzneimitteln¹⁾

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Synopsis — Solubilization of essential oils with polyoxyethylene glyceryl fatty esters. IV. The use of solvent couplers as auxiliaries in the preparation of pharmaceuticals. — The utility of POLYOXYETHYLENE GLYCERYL FATTY ACID ESTERS for the SOLUBILIZATION OF ESSENTIAL OILS was examined. The results with PEPPERMINT, LAVENDER, ANISE, and CLOVE OILS are represented with the aid of phase diagrams. The surfactants' ability to solubilize these oils improves when the carbon chain of the fatty acids is shortened and when the polyoxyethylene chain length is increased.

Die Solubilisierung ätherischer Öle besitzt u. a. für die Aromatisierung arzneilicher Liquida (1) sowie für Kosmetika Bedeutung. Da das Solubilisierungsvermögen für reine Wirkstoffe von deren physikalisch-chemischen Eigenschaften und der Art der Tenside abhängt (2) (3), sind Ergebnisse der Lösungsvermittlung von Reinsubstanzen nicht ohne weiteres auf Stoffgemische, wie z. B. ätherische Öle, übertragbar. Es ist daher notwendig, die Solubilisierbarkeit ätherischer Öle, die bis zu 50 Bestandteile enthalten können (4), jeweils experimentell zu untersuchen.

Für die Lösungsvermittlung ätherischer Öle mit Tensiden vom Typ der Polyäthylenglykol-sorbitanfettsäureester liegen Untersuchungen vor, deren Ergebnisse zum Teil als Phasendiagramme (5) (6) (7), zum Teil als kritische

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Mischungsverhältnisse (8) (9) dargestellt sind. Das Solubilisierungsvermögen von Polyäthylenglykol-glycerinfettsäureestern für ätherische Öle wurde bisher nur von Nowak (10) in Form kritischer Mischungsverhältnisse angegeben. Derartige Untersuchungen erlauben jedoch nur eine eingeschränkte Beurteilung der Lösungsvermittlung, da mit der Bestimmung des kritischen Mischungsverhältnisses lediglich ein kleiner Bereich der Phasendiagramme beschrieben wird. In den vorliegenden Untersuchungen wurde deshalb, trotz des erheblichen Arbeitsaufwandes, unter den verschiedenen Möglichkeiten den Phasendiagrammen der Vorzug gegeben.

Um mit einer begrenzten Zahl von Substanzen einen weitgehenden Überblick über die Eignung der Polyäthylenglykol-glycerinfettsäureester als Lösungsvermittler für ätherische Öle zu bekommen, wurden für die Untersuchungen vier ätherische Öle herangezogen, die zwei verschiedenen chemischen Verbindungstypen zuzuordnen sind: Pfefferminzöl und Lavendelöl bestehen im wesentlichen aus Monoterpenen, während Anisöl und Nelkenöl Phenylpropankörper enthalten.

Das Solubilisierungsvermögen der oberflächenaktiven Substanzen wurde durch Wassertitration ermittelt (6), die häufig für ölige Substanzen (5) (6) (11) (12) (13) oder auch für Feststoffe Verwendung findet (14) (15).

EXPERIMENTELLE UNTERSUCHUNG³⁾ DER SOLUBILISATION

Untersuchte Substanzen⁴⁾

Anisöl DAB 7, Lavendelöl DAB 7, Nelkenöl DAB 7, Pfefferminzöl DAB 7 (Firma Dragoco, Gerberding & Co, D-345 Holzminden).

Tenside (Fa. Th. Goldschmidt AG, D-43 Essen), nähere Angaben (1).

Ermittlung der Phasendiagramme

Die Phasendiagramme wurden nach der Methode der sogenannten Wassertitration (5) (6) (8) (16) (17) ermittelt: Ätherisches Öl und Tensid wurden in ein trockenes Becherglas eingewogen und mit einem Magnetrührer gründlich gemischt. Anschließend wurde diese Mischung im Wasserbad auf $20^{\circ} \pm 0,5^{\circ} \text{C}$ temperiert und unter langsamem Rühren tropfenweise mit destilliertem Wasser aus einer Bürette versetzt. Dabei wurde Einrühren von Luft möglichst vermieden.

³⁾ Für sorgfältige technische Mitarbeit danken wir Frl. U. Biehler.

⁴⁾ Den Herstellern der ätherischen Öle und der Tenside danken wir für die Überlassung von Untersuchungssubstanzen.

Während der Titration wurde der Ansatz im durchfallenden Licht beobachtet. Beim Auftreten von Trübungen oder starken Viskositätsänderungen wurde die zugegebene Wassermenge nur dann als Endwert angenommen, wenn die Änderung mindestens eine Minute erhalten blieb.

Die nach dieser Konvention bestimmten Grenzwerte des Diagrammes schließen eine begrenzte Schwankungsbreite endgültiger Phasen- oder Viskositätsänderungen nicht aus. Gleichgewichtseinstellungen in derartigen Systemen können mehrere Tage in Anspruch nehmen (16) (18). Die ermittelten Werte erwiesen sich jeweils als gut reproduzierbar.

Die Prozentanteile der einzelnen Komponenten, bezogen auf die Gesamtmenge der jeweiligen Mischung, wurden errechnet und in das Diagramm übertragen. Auf die Bestimmung mesomorpher Phasen im polarisierten Licht wurde verzichtet, da bei den vorliegenden Untersuchungen die praktische Anwendbarkeit der Tenside als Lösungsvermittler von Interesse war.

Ablesung von Phasendiagrammen

Bei der Ablesung der Dreiecksdiagramme ist davon auszugehen, daß der prozentuale Anteil der Komponenten auf den jeweiligen Parallelen zur Null-Linie aufgetragen ist. Diese Linie wird durch die entsprechenden Parallelen zu den anderen Grundlinien geschnitten, so daß auf diese Weise das Mischungsverhältnis an jedem beliebigen Punkt des Diagrammes bestimmt werden kann (19). Ein Beispiel liefert *Abb. 11*: Punkt P repräsentiert eine Mischung von 33 % Tensid, 5 % Wasser und 62 % ätherischem Öl.

ERGEBNISSE

Ätherische Öle mit Monoterpenen

Pfefferminzöl

enthält in der Regel:

4—12 % Mentylester (berechnet als Menthylacetat), mindestens 48 % Gesamt-D-Menthol (20), etwa 10 % Menthon, daneben Menthofuran und weitere Bestandteile wie Phellandren, α -Pinen, Cineol (4). Am Beispiel von Pfefferminzöl läßt sich die Eignung der verschiedenen Tenside als Lösungsvermittler aufzeigen.

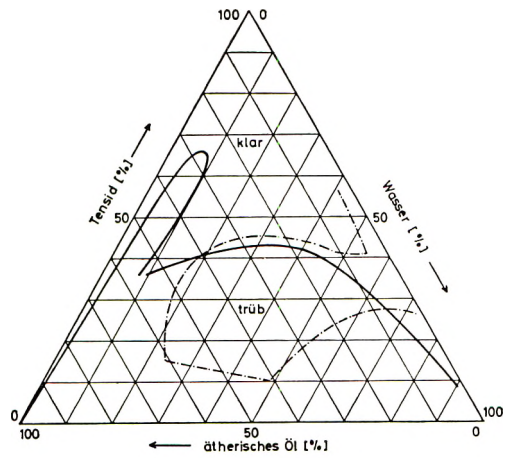


Abbildung 1

Phasendiagramm: Pfefferminzöl / Polyäthylenglykol(30)-glycerinlaurat / Wasser

— · — · — · — Bereich erhöhter Viskosität (~ 600 cP)

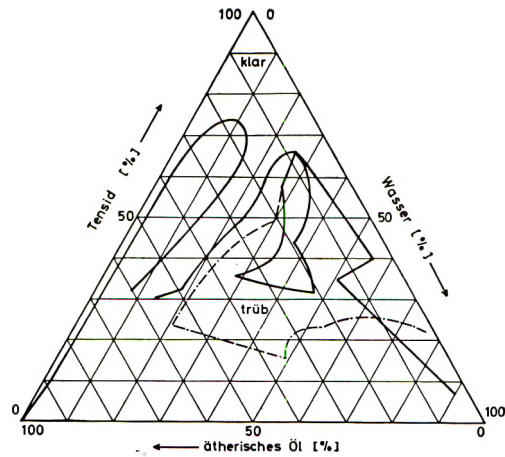


Abbildung 2

Phasendiagramm: Pfefferminzöl / Polyäthylenglykol(20)-glycerinoleat / Wasser

— · — · — · — Bereich erhöhter Viskosität (~ 4000 cP)

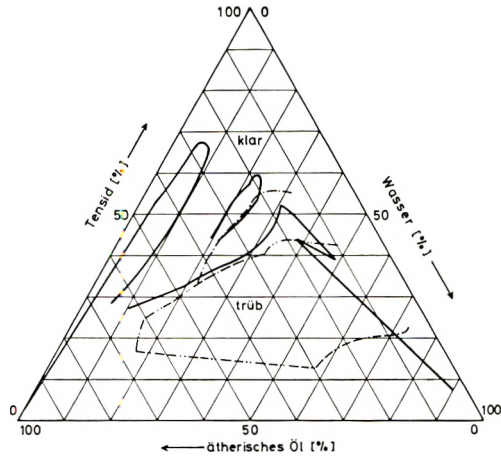


Abbildung 3

Phasendiagramm: Pfefferminzöl / Polyäthylenglykol(30)-glycerinoleat / Wasser

- - - - - Bereich erhöhter Viskosität (~ 600 cP)
- — — — — Bereich erhöhter Viskosität (~ 6000 cP)

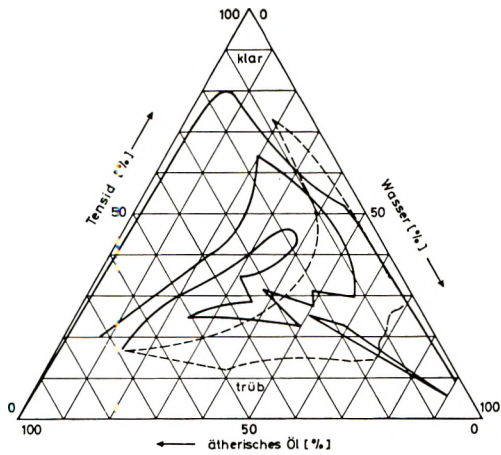


Abbildung 4

Phasendiagramm: Pfefferminzöl / Polyäthylenglykol(15)-polyglycerinricinoleat / Wasser

- - - - - Bereich erhöhter Viskosität (~ 1200 cP)

Mit zunehmendem Polyäthylenglykolanteil im Tensidmolekül wird das Solubilisierungsvermögen für Pfefferminzöl verbessert. Wie Abb. 1, 2, 3 und 12 entnommen werden kann, vergrößert sich der Bereich der Phasendiagramm-

me, in dem eine klare Mischung des Systems ätherisches Öl — Tensid — Wasser vorliegt. Dieser Verbesserung der Lösungsvermittlung durch einen erhöhten Polyäthylenglykolanteil steht der Einfluß der verschiedenen Fettsäurereste gegenüber: Die Laurinsäurederivate der Tenside eignen sich besser als die entsprechenden Ölsäureester (*Abb. 1* und *3* bzw. *Abb. 2* und *12*). Von allen untersuchten Tensiden verbessert Polyäthylenglykol(15)-glycerinricinoleat am wenigsten die Löslichkeit von Pfefferminzöl (*Abb. 4*).

Wie in den Phasendiagrammen dargestellt ist, können Bereiche erhöhter Viskosität auftreten; lediglich bei Polyäthylenglykol(20)-glycerinlaurat sind keine Viskositätsänderungen gleichen Ausmaßes feststellbar (*Abb. 12*).

Von den Erfahrungen ausgehend, daß sich die höher äthoxylierten Tenside besser zur Solubilisierung von ätherischen Ölen eignen, fanden für alle weiteren Untersuchungen nur Tenside mit dem Äthoxylierungsgrad 30 Verwendung.

Lavendelöl

enthält mindestens 33,4 % Ester, berechnet als Linalylacetat, daneben freies Linalool und geringe Mengen an anderen Terpenalkoholen und -ketonen. Insgesamt liegen etwa 30 Einzelbestandteile vor⁽²⁰⁾. Wie aus *Abb. 5* und *6* zu ersehen ist, gilt auch hier, wie bei Pfefferminzöl, daß sich das Laurinsäurederivat besser als das Ölsäurederivat für die Lösungsvermittlung eignet. Die korrespondierenden Phasendiagramme von Pfefferminzöl und Lavendelöl

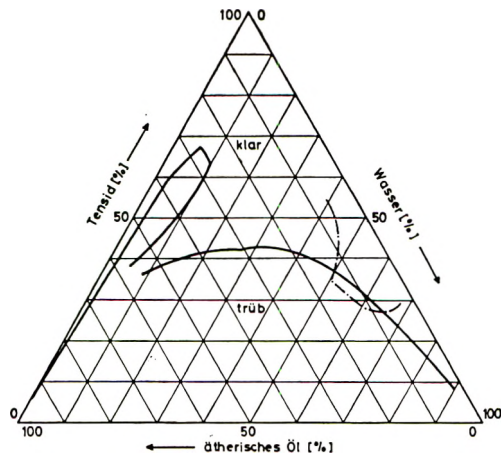


Abbildung 5

Phasendiagramm: Lavendelöl / Polyäthylenglykol(30)-glycerinlaurat / Wasser

--- Bereich erhöhter Viskosität (~ 600 cP)

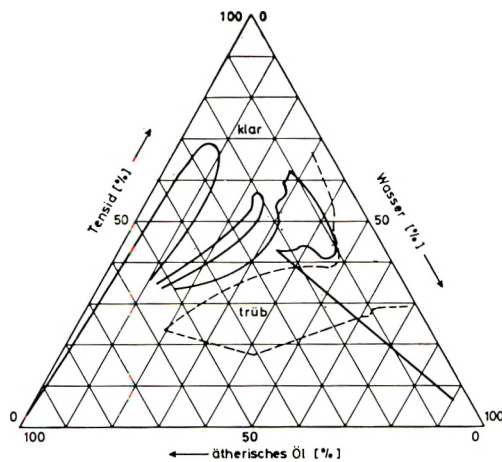


Abbildung 6

Phasendiagramm: Lavendelöl / Polyäthylenglykol(30)-glycerinoleat / Wasser

----- Bereich erhöhter Viskosität (~ 1200 cP)

sind quantitativ und qualitativ sehr ähnlich. Die Lavendelöl betreffenden Diagramme weisen jedoch verkleinerte Bereiche erhöhter Viskosität auf.

Ätherische Öle mit Phenylpropankörpern

Anisöl

enthält 80—90 % *trans*-Anethol, ferner Methylchavicol und *p*-Methoxyacetophenon (20).

Auch das Gemisch von Phenylpropankörpern wird durch Polyäthylenglykol(30)-glycerinlaurat besser als durch das homologe Oleat lösungsvermittelt (Abb. 7 und 8). Im Bereich gleicher Mengenanteile der Einzelkomponenten finden sich im trüben Mischungsbereich wiederum Zonen erhöhter Viskosität. Insgesamt läßt sich, wie die kleineren Zonen mit klaren Mischungen zeigen, Anisöl schlechter solubilisieren als Pfefferminzöl und Lavendelöl. Die Phasenübergänge zeigen in den Diagrammen einen sehr ähnlichen Verlauf.

Nelkenöl

Dessen Bestandteile sind ebenfalls den Phenylpropankörpern zuzuordnen, da es 80 bis 88 % Eugenol einschließlich Aceteugenol sowie Humulen, Caryo-

phyllen, Caryophyllenoxid und geringe Mengen verschiedener Alkohole, Aldehyde und Ketone enthält (20). Wie schon bei allen vorhergehenden Gegenüberstellungen, erweist sich auch hier Polyäthylenglykol(30)-glycerinlaurat dem entsprechenden Oleat etwas überlegen: Die Zonen mit klaren Mischungen

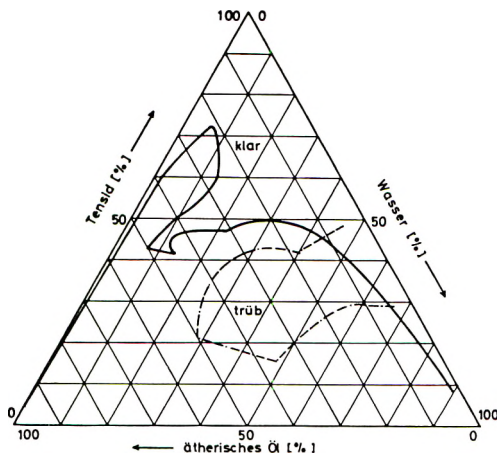


Abbildung 7

Phasendiagramm: Anisöl / Polyäthylenglykol(30)-glycerinlaurat / Wasser

--- · --- · Bereich erhöhter Viskosität (~ 4000 cP)

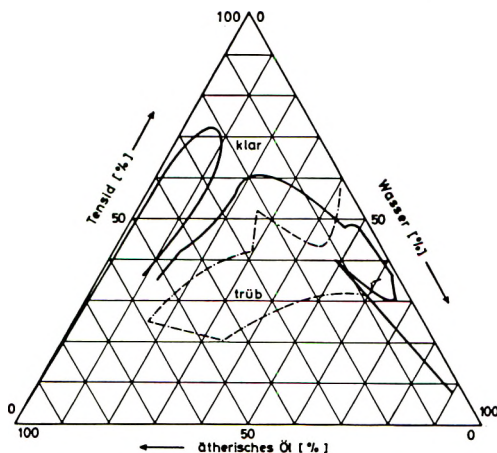


Abbildung 8

Phasendiagramm: Anisöl / Polyäthylenglykol(30)-glycerinoleat / Wasser

--- · --- · Bereich erhöhter Viskosität (~ 4000 cP)

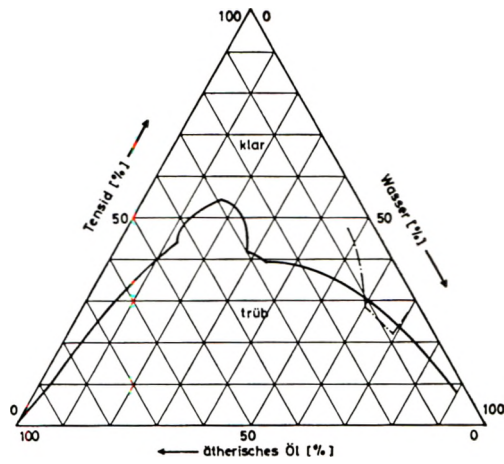


Abbildung 9

Phasendiagramm: Nelkenöl / Polyäthylenglykol(30)-glycerinlaurat / Wasser

--- Bereich erhöhter Viskosität (~ 600 cP)

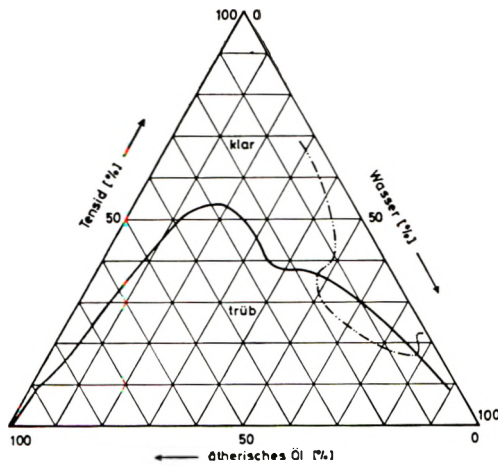


Abbildung 10

Phasendiagramm: Nelkenöl / Polyäthylenglykol(30)-glycerinoleat / Wasser

--- Bereich erhöhter Viskosität (~ 100 cP)

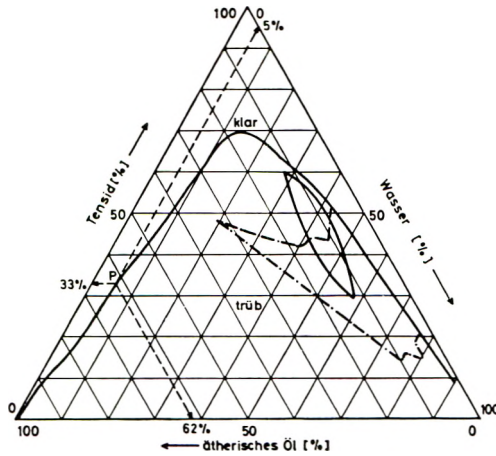


Abbildung 11

Phasendiagramm: Nelkenöl / Polyäthylenglykol(15)-glycerinricinoleat / Wasser⁵⁾

— · — · — · — Bereich erhöhter Viskosität (~ 600 cP)

sind nahezu gleich groß, der Bereich erhöhter Viskosität nimmt dagegen bei Polyäthylenglykol-glycerinoleat einen größeren Raum ein (Abb. 9 und 10). Das Ricinolsäureester-Tensid eignet sich für Nelkenöl ebenso wie für Pfefferminzöl am wenigsten zur Solubilisierung (Abb. 11).

Es ergab sich, daß Nelkenöl besser als die anderen ätherischen Öle durch Polyäthylenglykol-glycerinfettsäureester solubiliert wird. Wie aus Abb. 9 und 10 hervorgeht, nehmen die Zonen der klaren Mischungen jeweils die größte Fläche in allen Phasendiagrammen ein. Im Gegensatz zum Solubilisationsverhalten der anderen ätherischen Öle steht auch die sehr viel bessere Mischbarkeit ohne Trübung der Phasen im Bereich kleiner Wasseranteile von 3—10 %.

Charakterisierung der kolloidphysikalischen Zustände

Ausgehend von den durch Winsor (21) (22) entwickelten Vorstellungen lassen sich folgende Zustände am Phasendiagramm des Systems Pfefferminzöl/Polyäthylenglykol(20)-glycerinlaurat/Wasser beschreiben: Die linke Außenlinie des Phasendiagrammes repräsentiert binäre Mischungen aus Tensid und ätherischem Öl. Bei Zugabe von Wasser bewegt man sich vom Ausgangspunkt

⁵⁾ Die gestrichelten Linien dienen zur Veranschaulichung der Ablesung von Phasendiagrammen, siehe: Experimentelle Untersuchung der Solubilisierung.

auf einer Geraden in Richtung auf die rechte untere Ecke des Phasendiagrammes (100 % Wasser). Nach Zugabe geringer Mengen Wasser kommt es hierbei zunächst zu einer Solubilisierung von Wasser in ätherischem Öl (Abb. 12, Strecke AE und BF). Mit steigendem Wasseranteil bildet sich, falls das Solubilisierungsvermögen überschritten wird, eine W/O-Emulsion, welche bei niedri-

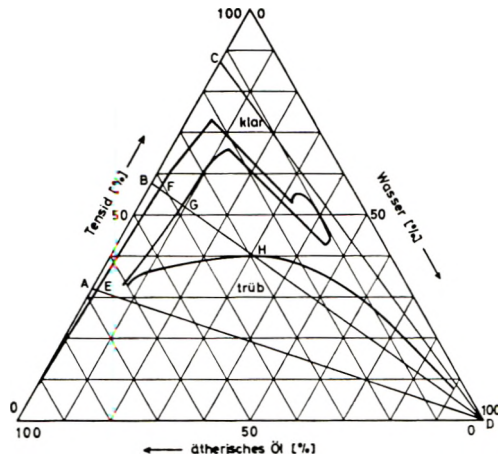


Abbildung 12

Phasendiagramm: Pfefferminzöl / Polyäthylenglykol(20)-glycerinlaurat / Wasser⁶⁾

gen Tensidkonzentrationen direkt in eine O/W-Emulsion übergeht (unterer Bereich der Trübung mit der Strecke ED). Bei hohen Tensidkonzentrationen bleiben nach Wasserzugabe von Beginn an klare Lösungen erhalten, wobei auf Mizellarer Ebene der gleiche Wechsel zwischen einer W/O- und O/W-Verteilung stattfindet (z. B. entsprechend der Strecke CD). Von mittleren Tensidkonzentrationen ausgehend, wird zunächst Wasser in Öl solubilisiert (Strecke BF). Darauf folgt ein Trübungsbereich, in dem das Wasseraufnahmevermögen des Systems überschritten ist (Strecke FG). Im weiteren Verlauf finden sich wieder ein Bereich ohne Trübung (Strecke GH) und eine Trübungszone (Strecke HD).

Unter geeigneten Bedingungen bilden sich in solchen Diagrammen erkennbare Zonen mit mesomorphen Phasen aus. Diese Erscheinung ist hauptsächlich für ionische Tenside beschrieben; sie wurde aber auch bei nichtionischen Tensiden beobachtet (12) (13) (23). Dieser besonderen Zustandsform liegt die Aus-

⁶⁾ Die Linien AD, BD und CD dienen der Erläuterung der kolloidphysikalischen Zustände im Phasendiagramm.

bildung lamellarer Strukturen zugrunde, welche optische Anisotropie bewirken. Auf den Nachweis dieser lyotropen, flüssig-kristallinen Phasen, welche aufgrund ihres Verhaltens im polarisierten Licht identifiziert werden können, wurde in den vorstehenden Untersuchungen verzichtet, da die Verwendbarkeit der Tenside als Lösungsvermittler im Vordergrund stand. Mesomorphe Phasen sind, wie vergleichbare Ergebnisse zeigen (12) (13) (23), im Bereich entsprechend etwa 50 % Tensidgehalt und 10 % Anteil der solubilisierten Substanz zu erwarten.

Die Natur der Zonen mit erhöhter Viskosität (*Abb. 1 bis 11*) ist nicht genauer differenziert. Diese können z. B. auf die Ausbildung hochviskoser Gele, wie sie bei der Mischung von Tensid und Wasser allein auftreten (24), oder auf das Entstehen fester Bestandteile, welche neben flüssigen Komponenten vorhanden sind (23), zurückzuführen sein. Sehr hohe Viskositäten machten es auch unmöglich, im Rahmen dieser Untersuchungen Phasendiagramme mit Polyäthylenglykol(30)-glycerinstearat zu gewinnen.

DISKUSSION DER ERGEBNISSE

Legt man als Beurteilungsmaßstab die Fähigkeit der Phasen, sich ohne Trübung zu mischen, den Diagrammen⁷⁾ zugrunde, so zeigen die Untersuchungsergebnisse, daß ätherische Öle um so besser solubilisiert werden, je höher der HLB-Wert der Tenside ist. Sowohl durch Verkürzung des Fettsäurerestes als auch durch Erhöhung des Polyäthylenglykolanteiles wird eine Steigerung des Solubilisierungsvermögens erreicht. Polyäthylenglykol(30)-glycerinlaurat war am besten geeignet (1).

Diese für ätherische Öle nachweisbare Beziehung zwischen HLB-Wert und Solubilisierungsvermögen der Tenside läßt sich nicht auf die Lösungsvermittlung von Glucocorticoiden übertragen. Die Fähigkeit von Polyäthylenglykol-glycerinfettsäureestern, ätherische Öle in Lösung zu bringen, entspricht etwa der von homologen Polyäthylenglykol-sorbitanfettsäureestern, wie sich aus vergleichbaren Untersuchungen mit Pfefferminzöl ergibt (6) (7). In Übereinstimmung mit früheren Ergebnissen (9) (17) (25) wurde durch die vorliegende Untersuchung bestätigt, daß ätherische Öle, die einen etwas polaren Charakter besitzen (Pfefferminzöl), besser solubilisiert werden können als ätherische Öle mit vergleichsweise weniger polaren Inhaltsstoffen (Anisöl). Lavendelöl ist ähnlich wie Pfefferminzöl einzustufen.

⁷⁾ Die Phasendiagramme wurden nach der Konvention von O'Malley, Pennati und Martin (6) erstellt. Da Gleichgewichtseinstellungen sich über mehrere Tage hinziehen können (16) (18), sind bei Lagerung noch gewisse Veränderungen des Verlaufs der Phasenübergänge möglich.

Im Gegensatz dazu läßt sich die bessere Solubilisierbarkeit von Nelkenöl und der veränderte Verlauf der Phasenübergänge jedoch nicht durch die Hydrophilie des Eugenols erklären. Vielmehr muß hier die Bildung eines Komplexes zwischen dem Polyäthylenglykolanteil der Tenside und der phenolischen Hydroxylgruppe sowie die anschließende Solubilisierung dieses Komplexes in Betracht gezogen werden (26).

Wie aus den Untersuchungsergebnissen abgeleitet werden kann, lassen sich die Unterschiede in der Solubilisierbarkeit nicht auf die verschiedenen, in ätherischen Ölen enthaltenen Stoffgruppen (Phenylpropankörper, Terpene) zurückführen, sondern auf funktionelle Gruppen, welche die physikalisch-chemischen Eigenschaften der Inhaltsstoffe stark bestimmen (z. B.: Alkohol-, Ester- und Ätherfunktionen).

Im Hinblick auf die Ergebnisse der Solubilisierung von Glucocorticoiden (1) und deren Lokalisierung in der Mizelle ist anzunehmen, daß der Solubilisierung der ätherischen Öle im wesentlichen eine Bindung an den Polyäthylenglykolgürtel der Mizelle zugrunde liegt. Dafür sprechen sowohl die Polarität der ätherischen Öle wie auch die Auswirkungen von Veränderungen an den hydrophilen und lipophilen Anteilen im Tensidmolekül. So unterscheidet sich das Solubilisierungsvermögen von Polyäthylenglykol(30)-glycerinlaurat und -oleat nur relativ geringfügig (*Abb. 1* und *3*), während die Reduzierung des Polyäthylenglykolgehaltes bei Polyäthylenglykol-glycerinoleat auf einen Äthoxyierungsgrad von 20 zu einer deutlicheren Verminderung der Fähigkeit, sich ohne zu trüben zu mischen, führt (*Abb. 2*).

Die zunehmende Herabsetzung der Solubilisierbarkeit von Lavendelöl und Anisöl beim Übergang von Polyäthylenglykol(30)-glycerinlaurat zu -oleat (*Abb. 5, 6* und *7, 8*) gestattet es, den Lokalisierungsbereich dieser Öle mehr im Inneren der Mizelle als bei Pfefferminzöl festzulegen. Ebenso muß eine Bindung des Polyäthylenglykol-Eugenol-Komplexes in der Polyäthylenglykohlülle der Mizellen angenommen werden, da die Veränderung der lipophilen Komponenten der Tenside nahezu keine Auswirkungen zeigt (*Abb. 9* und *10*).

Unterschiede in der Beurteilung des Solubilisierungsvermögens der Polyäthylenglykol-glycerinfettsäureester nach den Bereichen klarer Mischungen in den Phasendiagrammen und den kritischen Mischungsverhältnissen (10) resultieren aus der beschränkten Aussagekraft letzterer. Klare Mischungsverhältnisse bezeichnen lediglich das größte Mengenverhältnis Öl/Tensid, berechnet für 10 g Mischung, welches bei Verdünnung mit 90 Teilen Wasser oder mehr noch eine klare Lösung ergibt. Trübungszonen oder Bereiche der Viskosität, denen im Laufe der Wassertitration wieder klare Lösung folgt, werden daher durch kritische Mischungsverhältnisse nicht erfaßt.

Im Gegensatz dazu lassen sich jedoch diese kritischen Mischungsverhältnisse aus den Phasendiagrammen ablesen: Der 100⁰/₀-Wert für Wasser (\cong 0⁰/₀ ätherisches Öl) wird mit dem Schnittpunkt des Phasenüberganges klar/trüb und der 90⁰/₀-Linie für Wasser verbunden. Die Verlängerung dieser Geraden gibt auf der linken Außenlinie des Diagramms das kritische Mischungsverhältnis in Prozenten an.

ZUSAMMENFASSUNG

Die Anwendung von Polyäthylenglykol-glycerinfettsäureestern zur Solubilisation ätherischer Öle wurde untersucht. Die mit Pfefferminz-, Lavendel-, Anis- und Nelkenöl erhaltenen Ergebnisse wurden mittels Phasendiagrammen dargestellt. Die Fähigkeit von Tensiden, diese Öle zu solubilisieren, nimmt mit Verkürzung der Kohlenstoffkette der Fettsäuren und mit Verlängerung der Polyoxyäthylenkette zu.

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Recoating of Human Hair by Sebum

Dr. HANS EBERHARDT*

Synopsis—The results of two model experiments show that SEBUM does not creep along the HAIR. Accordingly, the sebum which coats the hair does not originate from its FOLLICLE. It is assumed that the terminal hair picks up sebum mechanically from surrounding follicles.

The hair and the SEBACEOUS GLAND together form the pilosebaceous apparatus in both man and hairy animals. The hair protects the body from loss of warmth, while the sebaceous glands protect the hair by covering it with lipid. Therefore, we can assume that the sebum, which is present in the hair follicle, is coating the whole hair. Greasing of the hair, which takes place during its growth out of the sebum-filled follicle, is of minor importance, since the rate of hair growth is only 0.35 mm a day. Moreover, recoating of hair by sebum occurs within a few days. Therefore, creeping of the sebum along the hair, as has been assumed by some authors (1), (2), seems to provide a natural explanation for the process of hair greasing.

INTRODUCTION

The Creeping of Sebum Along the Hair

The passive creeping of the sebum along the hair was examined in two experiments: the capillary experiment and the spreading experiment. These experiments will be discussed in the following two sections of this paper.

EXPERIMENTAL AND RESULTS

The Capillary Experiment

A glass capillary was filled with freshly sampled, human sebum, and a human terminal hair was threaded into the capillary. The temperature was held

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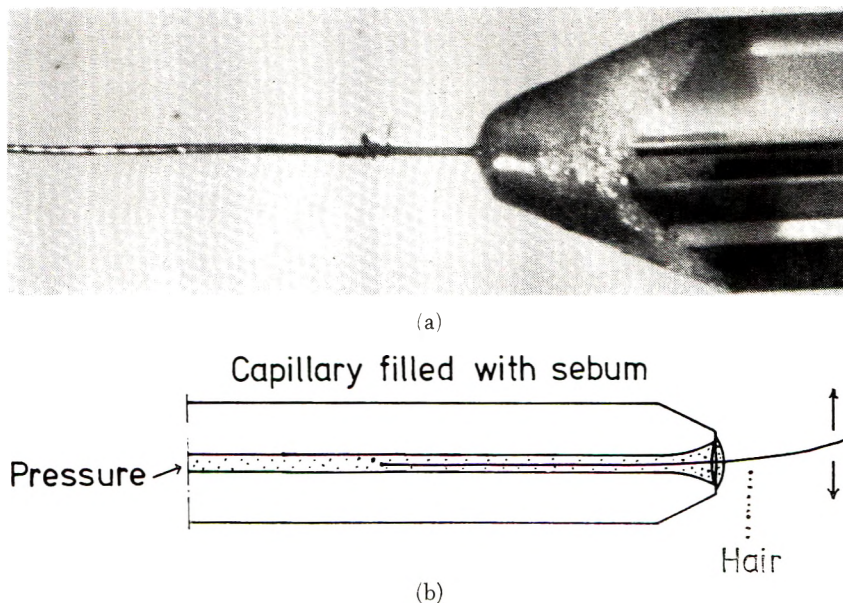


Figure 1. (a) + (b) Capillary experiment

constant at 35°C. Crystals of lipid soluble Sudan black were placed on the hair near the opening of the capillary to indicate whether or not any movement of sebum along the hair occurred. If sebum had crept along the hair, the Sudan black would have dissolved and colored the hair. This is shown in Figs. 1 (a) and (b).

Actually, the hairs remained unstained even after several days. In a modified experiment, the pressure on the sebum in the capillary was raised to enlarge the surface of the sebum in the funnel-shaped opening. Moreover, the hair was moved mechanically to imitate its natural movement. But again, the crystals did not dissolve. No creeping of sebum could be detected, and the hair did not function as a wick in the follicle.

The Spreading Experiment

To determine whether or not sebum spreads on human hair, a second experiment was conducted as follows.

A droplet of freshly sampled human sebum was placed on a human terminal hair, and the temperature was kept constant at 35°C, as is shown in Fig. 2. The droplet of sebum did not spread over the hair even after several days, and the size of the droplet did not change. This is identical with the behavior of lipids on textile fibers (7). Therefore, one may conclude that sebum

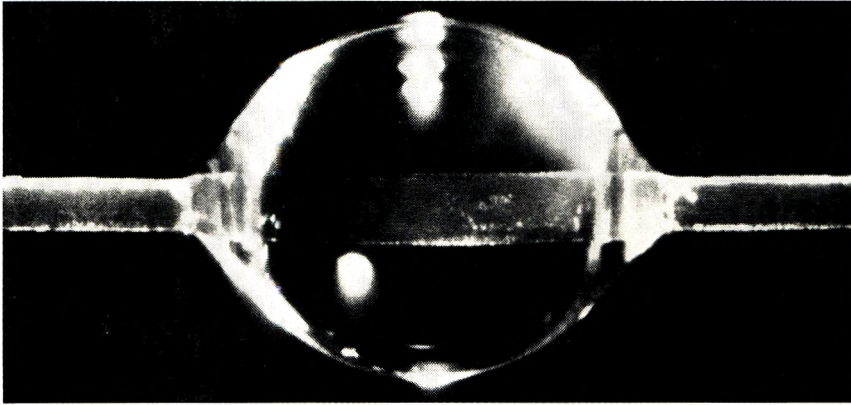


Figure 2. Spreading experiment

cannot spread along the hair and that greased hair is not greased by sebum from its own follicle. In other words, one can conclude that the sebaceous gland is not able to secrete sebum actively on the hair. A wick effect between parallel hairs may occur, but this is not the normal situation, because the distance between the hairs on the scalp is too large.

The Coating of Hair by Sebum

It is assumed that the hair picks up sebum mechanically from the surrounding follicles. Because this process occurs separately for each hair after each shampooing and is easily disturbed by external influences like combing, it is very difficult to establish the uniformity of this process. Two observations are reported, as follows, which support our assumption concerning the mechanism of the sebum coating of hair.

Lack of Lipid on the Hair

Terminal hairs from a normally oily scalp are extracted and pressed on a glass plate. After removing the hair from the plate, the lipid prints of the hair are visible on the plate. This is illustrated in Fig. 3.

Some, but not all, of this head's oily hairs show a reduction or even a lack of lipids for about 1 to 2 cm from the root of the hair. Obviously, the hair is able to pick up sebum from follicles at a distance of 1 cm or more from its own follicle.

This observation can be readily explained because hair does not grow parallel to the skin surface. There is always an angle between the hair and the surface. This angle depends on the length and, most probably, on the thickness of the hair. The hair may touch the skin surface again after a distance of 1 cm or more, where it can pick up sebum from neighboring follicles.



Figure 3. Lack of lipid on hair

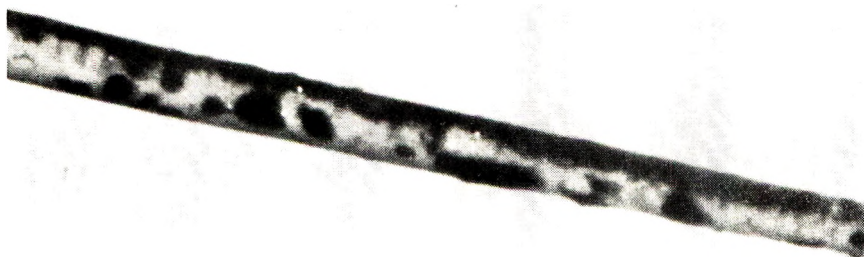


Figure 4. Lipid pattern on oily hair

Lipid Pattern on Oily Hair

White or blond hairs, which were extracted from human scalps, were exposed to an atmosphere of osmium tetroxide. After a few minutes, the lipids on the hair were stained black as is indicated in Fig. 4.

When examined under a stereoscopic microscope, these oily hairs showed a droplet-shaped pattern of lipids on the greasy areas as a result of the adsorption of sebum from the follicles. No coherent film was visible which would be evidence of the spreading of sebum over the hair.

CONCLUSIONS

Hair is oilier, if it is pressed against the head, e.g., by a hat. Persons with upright hairs exhibit only greasy scalps not greasy hairs. Short hair is recoated by sebum more slowly than long hair.

The time for the regeneration of lipid on the forehead is very different from the time needed for the greasing of hair. We were able to demonstrate that the greasing of hair occurs within a few days (3). Measurements with the same method revealed that the regeneration of lipid on the forehead is completed within a few hours and that it is stopped by a regulatory mechanism (4). We were also able to demonstrate that the lipid regeneration time of skin

on the forehead is the same as that of skin on the scalp (5). Hair can then pick up sebum from the oily skin until it is saturated with the lipid (3). This level is reached after a few days.

The greasing mechanism of hair after shampooing may then be described as follows: after it is degreased by shampooing, the follicle is filled with sebum until regulation by surface tension occurs. The hair in the follicle has no effect on this regulation because it does not change the surface area of the sebum in the follicle. It was shown by Kligman and Shelly (6) that follicles filled with sebum look like oily pools. The pools of strong excretors contain more sebum than those of weak excretors (4). The hairs pick up the sebum from these pools mechanically, i.e., by simple contact with the scalp, until the hairs are saturated with lipids. During greasing and in the steady state, sebum transfer from hair-to-hair, hair-to-skin, and skin-to-skin is also possible. When the hair cannot pick up any more sebum, the excretion of sebum is stopped by surface tension.

Therefore, we conclude that the lipid pick up by hair is not regulated active by a special mechanism. The hair loses its sebum naturally, and continually picks up small quantities of sebum from the follicle and causes a weak but steady excretion of sebum on the hairy skin. This is the natural function of the sebaceous glands.

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Book Reviews

TASCHENBUCH DER MODERNEN PARFÜMERIE UND KOSMETIK, von Hugo Janistyn, 4., neubearbeitete Auflage, XIII, 833 Seiten, zahlreiche Tabellen, Kunststoffeinband. Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart 1974. Preis: DM 165,—.

Infolge stofflicher Erweiterung und neuer technischer Gestaltung ist die Kennzeichnung dieser Publikation als Taschenbuch eine Untertreibung. Inhaltlich ist es, verglichen mit dem dreibändigen „Handbuch der Kosmetika und Riechstoffe“ (Dr. A. Hüthig Verlag, Heidelberg 1969-1973) des Autors, ein, allerdings umfangreicher, Auszug dieses Werks. Insofern kann es nicht überraschen, daß die Beurteilung des Taschenbuchs mit der des Handbuchs weitgehend übereinstimmt. Solche Wiederholung von Argumenten zur Beurteilung eines Fachbuches ist aber nützlich, um die Kontraste innerhalb des Faches stets erneut in Erinnerung zu rufen. Der Autor ist meines Erachtens, wie schon oft vermerkt, Empiriker, der Kosmetika kritisch, häufig genug mit Miß-

trauen und kaum verhüllter Ironie begutachtet, worin ihm angesichts der in vielen Fällen geradezu leichtfertigen, wie man dann entschuldigend behauptet, „dichterisch“ übertreibenden Werbung recht zu geben ist. Jedoch sieht — laut dem der 3. Auflage dieses Buches entnommenen Vorworttext — der Autor die in vielen Ländern gesetzlich definierten Grenzen des Aufgabenkreises der Kosmetik gegenüber Medizin und Pharmazie in Wirklichkeit als verschwommen an. Er läßt überhaupt gegenüber den von ihm übrigens leider als Synonyme gebrauchten Begriffen Kosmetika und Kosmetik (darin vielen Fachleuten gleichend, was aber die Synonymie nicht richtiger macht) eine deutlich zwiespältige Meinung erkennen. Diese Unsicherheit charakterisiert er vor allem im „Schlußwort“ (p. 756, aber auch schon p. 215 f.) recht klar, dessen Ausführungen tiefen Pessimismus vermitteln. Die von mir gelotete Tiefe seines Pessimismus ist dem Autor vielleicht gar nicht bewußt und nur Folge der Verkennung neuer Bemühungen um den Sinngehalt der Kos-

metik. Es spränge den Rahmen einer Rezension, darauf näher einzugehen. Entschieden widerspreche ich wegen der Wiederholung der schon im Vorwort zur 3. Auflage geäußerten Ansicht, Kosmetik könne nicht als selbständige Wissenschaft betrachtet werden, ist sie doch die Behandlung des Menschen mit chemischen Mitteln zur Optimierung seines Aussehens. Die Anwendung der Kosmetika setzt Forschung voraus und insofern erscheint sie als ein in einer umfassenderen Disziplin abgrenzbarer Teil. Dieses Verhältnis gleicht dem der therapeutischen Forschung als Wissenschaft zur Medizin. — Der Autor verfügt über eine mit größtem Fleiß angelegte enorme Materialsammlung. Es ist daher sehr zu bedauern, daß er diese Stofffülle nicht exakt genug systematisierte. Die zitierte Literatur ist leider ungenügend berücksichtigt, vor allem was die neuere betrifft. Arbeiten bis 1973 in größerem Umfang erfaßt, würden dem Benutzer gute Dienste leisten. Eingehendes Studium mancher dieser Arbeiten hätte des Autors Fachpessimismus gemindert. — Die Verarbeitung so umfangreichen Materials ist selten frei von Irrtümern zu halten. So wäre z. B. anzugeben gewesen, daß Natriumperborat (p. 224) nur eine handelsübliche Bezeichnung sowohl für Natriotetraborat-Wasserstoffperoxid-9-Wasser ($\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}_2 \cdot 9 \text{H}_2\text{O}$) als auch für Natrioperoxoborat-trihydrat oder Natriometaborat-Wasserstoffperoxid-3-Wasser ($\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3 \text{H}_2\text{O}$) ist, das allein angeführt wird; unter „Natriumperborat“ (p. 233) finden sich Angaben, die teils von den auf p. 224 mitgeteilten verschie-

den, teils Wiederholung sind. — Zu „Kaliumjodid“ (p. 229) wird ausgesagt, das Jod-Ion wirke regenerierend, aber nicht worauf. Die Verwendung des Salzes zur Erzielung von Abmagerung durch extern-lokale Applikation (auch von Oleyljodid) nimmt jedoch der Autor erkennbar nicht ernst. — Die Qualität des Buches wird durch kritische Bemerkungen, wie z. B. im in der neuen Auflage hinzugefügten Abschnitt „Die Herrennote“, mitbedingt, wenn der Autor auf die Tatsache verweist, daß die als männlich gemäß herrschenden Vorstellungen bezeichneten Gerüche gerade die Frau anzusprechen haben. Der Begriff Herrennote ist genau genommen verschwommen (p. 214). Ein weiteres Beispiel ist die Stellungnahme des Autors zu pflanzlichen Drogen und Wirkstoffen (p. 344). Er wundert sich, weshalb die doch offenbar leicht zugänglichen Stoffe, die beim Welken von Pflanzen (laut Filatow) entstehen, noch nicht identifiziert worden sind. Die innerliche Wirkung pflanzlicher Drogen einer äußerlichen gleichzustellen, wie dies von Kosmetikerinnen und leider selbst von größeren Firmen praktiziert wird, betrachtet der Autor als unsinnig. Er fragt zugleich, wieso man Kosmetika mit Pflanzenextrakten „biologisch“ nennen darf und bezeichnet eine derartige Aussage als grobe Irreführung. — Alles in allem kann ich für diese Auflage mein Urteil über die 3. Auflage dieses Buches (vgl. Parfümerie und Kosmetik 47, 276 [1966]) wiederholen: Das Taschenbuch ist mit gutem Gewissen zu empfehlen.

Hans Freytag, Darmstadt

CHEMICAL PROCESS ECONOMICS, Vol. I, 2nd Ed., Edited by J. Happel and D. G. Jordan. Marcel Dekker, Inc., New York, 1975. 511 pages. Price \$19.75.

This is the first volume in a new international series of chemical processing and engineering textbooks. Volume I examines the economic factors that influence project analysis and plant design in detail.

In Chapter I, in detail we are given an introduction to the Chemical Industry. The effects of raw materials, energy, and manpower requirements on chemical production, and research development expenditures are covered. The financial aspects of the Chemical Industry, including the small to large companies, are discussed.

Chapters II, III, and IV are concerned with the principles of economic evaluation. The inclusion of basic economic concepts in Chapter II should be helpful to many engineers involved in cost estimation and project analysis. Rate of return, cash position, income taxes, investment position, net profits, cost of product, and pay-out time are just a few of the topics treated in this chapter. Each point is illustrated through the use of problems, which cover simple through complex situations.

Chapter III gives a detailed discussion of the various economic evaluation equations that are useful in preparing an economic evaluation.

Chapter IV presents a discussion of the more advanced mathematical techniques used in the evaluation and analysis of project feasibility. Many of these advanced techniques are readily handled by computers, a

point not adequately covered by the authors.

Chapters V and VI provide information which enable the reader to apply the techniques previously discussed. The difficult topic of cost estimation is covered briefly; the authors leaving a detailed explanation of this to other texts in the field.

The remaining two chapters are involved with project analysis and process plant components. Design of distillation columns, heat transfer apparatus, and piping are covered.

All chapters are generously referenced (146 references in all), and well illustrated with charts, diagrams, and problems. This book should be included in the Chemical Engineers' library and should be of considerable value.—GERALD ROYE—Chesebrough-Pond's Inc.

FRAGRANCE TECHNOLOGY—SYNTHETIC AND NATURAL PERFUMES, by Ronald W. James. Noyes Data Corporation, Park Ridge, New Jersey, 1975. 11 Introductory pages, 298 pages, 9 pages book advertising. Price \$36.00.

This book is a compilation of U.S. Patents since 1964 which relate to the manufacture of synthetic and natural perfumes and which are grouped according to odor type (i.e., woody, musk, floral), general processes, and product applications. This book encompasses a total of 246 patents. Each patent is summarized, and in most cases, pertinent examples are quoted from the patent. The summaries are, in general, well-prepared, and the examples are selected from the patents to cover the most important products or processes.

The author has selected a representative group of patents in the fragrance field. Consequently, the book should be especially useful to anyone who wants to make a quick survey of the recent developments in the fragrance technology covered by patents. No comments are made on the industrial importance of the patents, nor are there any references to the scientific literature. The book is, therefore, only a compilation of selected patents with summaries of inventions and examples taken from the specifications.

A table of contents at the front lists each patent and serves as a subject index. This book is also indexed by company, inventor, and U.S. Patent number. This arrangement should facilitate the locating of a patent in the book.

A similar volume authored by M. Gutcho was published in 1970 by Noyes Data Corporation under the title, "Chemical Process Review No. 45, Synthetic Perfumery Materials." It is essentially the same in organization and scope as the present volume, but covers an earlier period (1951-1970). A number of patents are included in both volumes. The basis for selecting patents for either volume is not clear to this reader. It would seem that a small supplement would have sufficed to update "Review No. 45," rather than this new volume.—NORMAN L. GREIF—Givaudan Corporation.

THE PHYSIOLOGY AND PATHOPHYSIOLOGY OF THE SKIN. Vol. III, Edited by A. Jarrett. Academic Press, New York, 1975, Price \$34.50.

Volume I of this series was on the epidermis and Volume II was on the

nerves and blood vessels. This series of books is aimed at bringing together contemporary knowledge and thinking on normal and abnormal skin physiology in a form such that the practicing dermatologist, biologist, and other scientists can relate it to some of the clinical problems each encounters.

This volume concerns itself with the dermis and the dendritic cells of the epidermis. The first section, on the dermis, gives an account of the chemistry of collagen and elastic tissues. The physical nature of the dermis in the living skin is discussed in some detail. Diseases affecting collagen and elastic tissue are described from the standpoint of their pathogenesis and pathophysiology.

There is also a chapter on the comparative physiology of the dermis and the relationship between its function and physical characteristics in different animals and body sites. Special reference is made to melanocytes and its pathology in pigmentary disorders of human and animal skin.

Some of the sections of particular interest to the cosmetic chemist are those on the chemistry and molecular biology of collagen; the physical nature of the dermis and the elastic tissues in living skin; dermal cell populations and their pathological responses; melanin and melanocytes; and the biochemistry of pigment formation.

The chapter on ageing of the dermis is of special interest. This chapter reviews skin thickness and an instrumental technique of charting it; the physical and physiological changes that occur with age; the

collagen cross-linkage theory; the changes in the glycosaminoglycan content; and the endocrinology of ageing skin.—H. Y. SAAD, Ph.D.—American Cyanamid Co.

HANDBOOK OF MOISTURE DETERMINATIONS AND CONTROL, PRINCIPLES, TECHNIQUES, APPLICATIONS, Vol. 2, by A. Pande. Marcel Dekker, Inc., New York, 1975. XV + 318 pages. Price \$33.50.

This volume constitutes four of 15 chapters (5 through 8), which will appear in four volumes utilizing continuous pagination. The index will appear in volume 4, thus limiting access to specific items without the availability of the set. This reviewer has not had access to these other volumes.

The four chapters of this volume are titled "Electrical and Electronic Methods;" "Spectroscopic Methods and Techniques;" "Nuclear Methods and Techniques;" and "Automatic Control of Moisture." All pages are photo-offset from the original typewriter prepared manuscript. There is no attempt to relate to any specific industrial area, but rather, the examples are taken to illustrate the procedure without concern to the material in which the water is present. Each method description is well-written and explains the principles and procedures without excessive detail. For those who want a basic understanding of the multitude of instrumental techniques available, this is very readable and informative. Indeed, solutions to unique individual problems may become obvious to the reader.

Unfortunately, few references after 1965 are to primary sources,

but are rather to books or reviews after this date. The extensive references are mostly earlier than 1965.

As stated, this book is an excellent source for any scientist who desires to obtain a good background in all principles of nonchemical water determination. It is especially commended to anyone having a problem in finding a suitable assay for a system not amenable to routine procedures.—JOHN H. WOOD—School of Pharmacy, Virginia Commonwealth University.

PERFUMES, COSMETICS, AND SOAPS, Vol. 1, THE RAW MATERIALS OF PERFUMERY, by W. A. Poucher, revised by George M. Howard (8th Edition). Chapman & Hall, London and John Wiley & Sons, New York. 381 pages. Price \$24.00.

If this book is not the Bible of the perfume industry, it is at least one of its important chapters. This 8th edition of "Poucher's" is a complete revision of the earlier perfumer's classic. It is in consonance with the modern world of the cosmetic. Many new materials have been added, and older obsolete materials have been deleted. A system of cross-referencing links the accepted chemical nomenclature to the terms of present usage.

A considerable number of formulas are presented for floral scents and bouquets. Processes are described. A few illustrations are presented.

All in all, this new edition is recommended as a useful up-to-date reference book.—CHESTER J. DE ZEIH—Valjean Corporation, Florida.

THE PRODUCTION, MANUFACTURE, AND APPLICATION OF PERFUMES, 8th Ed., Vol. 2, by William A. Poucher, Chapman and Hall, London, Halsted Press, John Wiley and Sons, New York, 1974. VIII + 379 Pages, indexed. Price \$24.00.

This presentation by Mr. Poucher is concise, neatly outlining some aspects of perfumery. The Cosmetic Chemist is usually not directly concerned with many of these in the course of his day-to-day responsibility; nonetheless, it is worthwhile for him to take time to become acquainted with information of this type.

Over the years, various historical sketches have been published. The opening chapter again reviews some of these sketches in brief form. The production of perfume gives an insight into methods of manufacturing that are of a passing interest to the cosmetic chemist. Purchase of these materials provides nothing of interest.

The author's odor classification was originally presented to the Society when he received the SCC Medal Award in 1954. It is dated, but nevertheless, worthy of attention, since it provides a facet with which most Cosmetic Chemists are unfamiliar.

The main thrust of the book deals with the monographs on flower perfumes. Each flower is defined, as to its source and area of origin. The material concerning odor classification, production, and the chemistry is minimal, and it is a disappointment that this information has not been more fully developed. The compounding notes are very interesting, but dated in today's climate

of increasing dependence on synthetics. For those who have a limited or have no background at all in perfumery, it does provide a basic insight. The chapters referring to jasmine, lily, orange blossom, violet, and especially rose, go into more detail and, perhaps, more of this book should have been comprised of similar information.

The chapters which deal with fancy perfumes, toilet waters, and soap perfumery do little more than outline additional formulations, again, most of which do not have a place in today's creative climate. The chemistry and odor description is once again lacking in these chapters. These three chapters do provide, however, information which the Cosmetic Chemist seldom sees. The closing chapters, which are concerned with tobacco flavors, floral cachous, incense and fumigants, sachets, solid perfumes, and fruit flavors provide very little of significant interest.

In general, this volume is interesting to read. Although not a must to include in one's library, it is worthwhile volume that provides information of value.—JOSEPH H. KRATOCHVIL—Firmenich Inc.

PERFUMES, COSMETICS AND SOAPS, Vol. 3, by W. A. Poucher, revised by G. M. Howard. Halsted Press, New York, N.Y., 1974, 465 pages illustrated, indexed. Price \$24.00.

The venerable Poucher has not been revised since 1960; the current edition is the 8th edition. The new author tells us that this is a complete revision. Certainly, it is nearly double in pages. The chapters, 14 alto-

gether, are arranged alphabetically, as they were in the original work. The new chapters cover aerosols, antiperspirants and deodorants, depilatories, and also include a men's toiletries chapter, which is the new title for the earlier work on shaving preparations. Chapters on smelling salts and theatrical requisites were dropped.

Author Howard states in his preface that the outstanding feature of Poucher's work is readability with the subject matter stripped of pseudoscience or advanced technology. This was certainly true of Poucher, even if it meant being outdated. Howard's aim is to continue the pattern of his predecessor . . . but updated.

When Poucher was written originally, cosmetic practice was not a science. It is today, however. To avoid the deeper discussions of the science behind cosmetics takes a bit of doing. Author Howard has quite successfully emulated Poucher.

British spelling and terminology stamp the origin of the work. There are a few misspelled words, at least one printer's error. The references are few and mainly dated. They appear in the text proper.

One must fault the manufacturing editor for style, lack of headings, and split formulas. The type is readable.

Howard's writing is amazingly faithful to the Poucher style, even to the continued use of some now suspect materials in the amounts found in formulations. This particularly refers to boraz, bithional, phthalates, and the parabens used along with ethoxylates. Cautions in the use of some finished products, which may yet not be mandatory in England, but are increasingly becoming important in other countries, are not included. One questions the mention of gums karya, tragacanth, and zinc oxide in depilatories. The aerosol chapter is condensed, possibly a bit too much. The chapter on hair dyes is weak. The bromo acid solution (described on page 204) is unique.

Being a sole author of a book enables one to have complete control at all times. However in today's climate, few of us, no matter how long our tenure in the cosmetic industry, can cover all fronts. So while this revision is certainly better than the original work, it does suffer from this deficiency.—M. G. DENAVARRE—Vanda Beauty Products.

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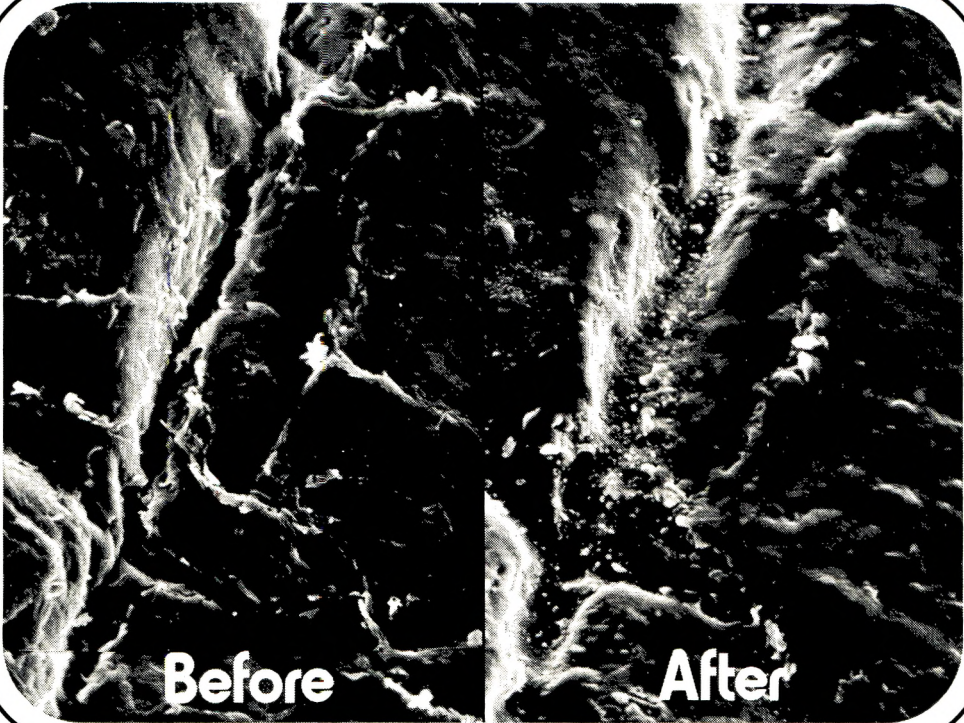
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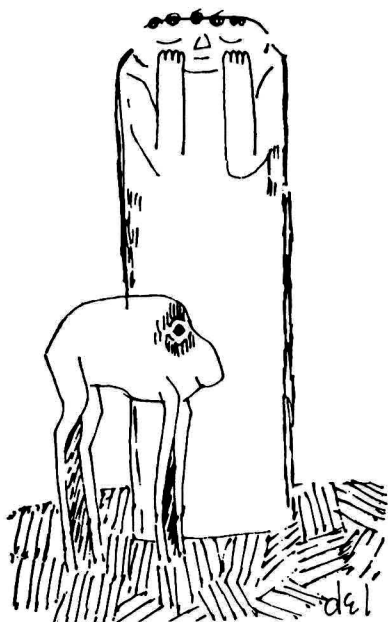
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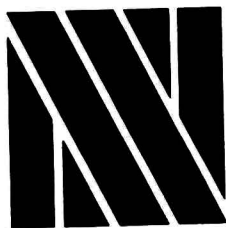
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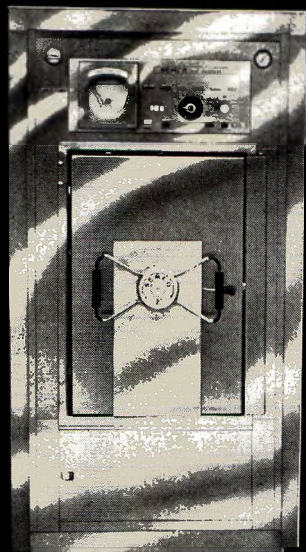
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