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Water-Absorptive Properties of Selected Solids in a Lipophilic Base I

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Abstract □ Water-absorptive properties of various combinations of starch, pregelatinized maize starch, talc, and zinc oxide dispersed in light liquid petrolatum were investigated. The suction force and mercury rise were measured in terms of millibars with a tensiometer. The performance of these dispersions was evaluated in terms of two estimated parameters, $\hat{\alpha}$ and $\hat{\beta}$, which were related to absorption rate and absorptive capacity, respectively. Water-absorptive capacity varied in a predictable way while absorption rate did not. Zinc oxide had the highest absorptive capacity. Some interaction among the powders was noted by a decrease in suction force when various ones were mixed together.

Keyphrases □ Water absorption—solids in lipophilic bases □ Tensiometry—absorption analysis □ Powder interaction—absorption effect □ Absorption model—solids in lipophilic bases □ Diagram—tensiometer

The USP (1) describes pastes as preparations which are more absorptive than ointments due to a higher concentration of powdered medicaments. These pharmaceutical preparations often contain starch, talc, and zinc oxide in addition to other absorbants. They are used, in part, on the skin for absorbing water or exudation resulting from various skin diseases. One of the needs of the dermatologists is a paste which has a desiccant effect for treatment of exudatory dermatoses.

It would, therefore, be desirable to know which powder or combination of powders will be the most effective absorbant in a particular base. Rae (2, 3) reported on a method of testing absorption by various ointment bases as well as results for individually dispersed solids in a water-soluble base. This method was dependent upon the passage of water through a cellulose film and being absorbed by the particular powders.

Other methods used for measuring water absorption by ointments involved addition of water from a buret and mechanical treatment (4, 5), urea adduct method

(6), and by drying loss, xylene distillation, and Karl Fischer titrimetric method (7).

The purpose of this research was to determine the absorptive powers of varying proportions of selected solids in a lipophilic base by utilizing a new method and procedure.

EXPERIMENTAL

Materials—The following materials were used for this experiment: starch, USP; pregelatinized maize starch¹; talc, USP; zinc oxide, USP passed through No. 60 sieve; light liquid petrolatum, NF. The pregelatinized starch is a modified waxy maize starch which has instant swelling in cold water to produce clear dispersions. The moisture content of the dried starches never exceeded 5%.

Instrumentation and Methods—Tensiometers have been used since the 1920's to measure the absorbing power and suction force of soils (8-11). In its basic form, a tensiometer consists of a porous ceramic cup containing water in equilibrium with the water in the colloid (soil) surrounding, and in contact with, the cup. A mercury manometer connected to the cup measures the pressure (tension) with which the water in the cup is held. The experimentally measured quantity is the pressure difference, in millibars, across the porous wall of the cup.

Figures 1 and 2 show pictorial views of the instrument while Fig. 3 illustrates the essential parts of a tensiometer.² A porous ceramic cup, filled with air-free water, is attached to a connecting tube, which is in turn connected to a manometer or a vacuum gauge. Water in the surrounding medium is in hydrologic contact with the water inside the cup through the pores of the wall. As water is drawn through the cup wall, the depletion of water in the cup is reflected by changes in mercury level of the manometer.

Since the mercury manometer measures tensions (negative pressures) relative to atmospheric pressure, the maximum reading theoretically possible would be 1 atm. (1,013 mbar.). Very few tensiometers are reliable above 850 mbar., however. Other characteristics of tensiometers further limit their usefulness in measurements of water

¹ Instant Clearjel, National Starch and Chemical Corp., New York, N. Y.

² Tensiometer 6", cat. No. 2600 A, Soil Moisture Equipment Co., Santa Barbara, Calif.

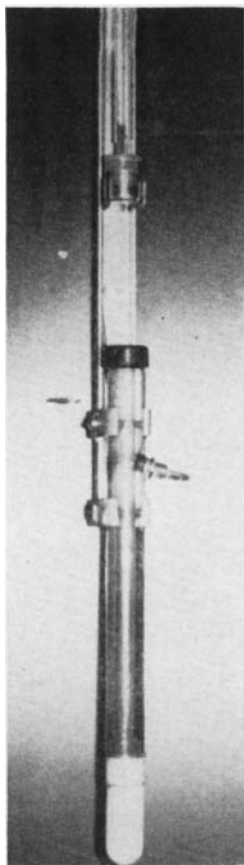


Figure 1—Pictorial view of tensiometer and mercury manometer. tension. Two of these, temperature and osmotic effects, are of greater consequence than most others. Inasmuch as the temperature of the medium and the instrument will influence manometer readings of pressure, care must be taken to maintain temperature constant during any given series of experiments. Osmotic gradients

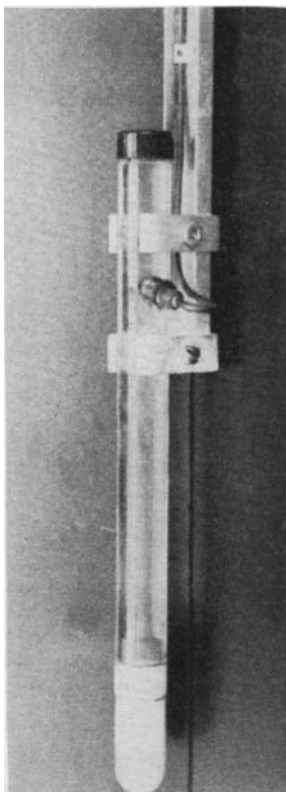


Figure 2—Close view of tensiometer.

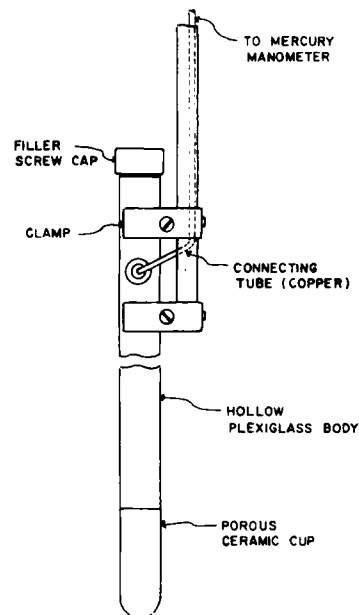


Figure 3—Tensiometer showing porous cup detail.

produced by dissolved salts in the material being evaluated are not measurable with tensiometers, because the ions in solution readily diffuse through the porous walls of the ceramic cup.

Five hundred grams of the dispersion were prepared by mixing 40% w/w of solid or combination of solids and 60% w/w light liquid petrolatum, NF. The dispersion was mixed for 5 min. with the aid of an electric mixer³ at a rate of 475 r.p.m. Combinations of solids were initially blended for 15 min. in a blender⁴ before dispersing in the base.

Four manometers were brought to zero by keeping the porous pots immersed in distilled water. This zero point varied slightly from day to day due to differences in temperature. The water was removed from the 50-ml. beakers and they were filled with the experimental dispersion. Excess water was sponged from the tips of the porous cups before immersion into the dispersions. The excess dispersion was allowed to overflow, and the apparatus was not disturbed during the absorption time period.

Readings were taken during regular intervals up to 8 hr., or until the mercury approached the maximum of 850 mbar. Utilizing a second portion of the experimental dispersion, the experiment was conducted again after a 24-hr. lapse. This experiment was designed in order to determine if a lapse of time had any effect on the water-absorptive powers of the selected solids.

STATISTICAL ASPECTS OF THE INVESTIGATION

Design of the Experiment—Since there was no *a priori* reason to favor any particular combination of powders, the design was chosen so that each powder was treated symmetrically. It was felt that this would enable the rendering of a fair judgment.

Throughout the remainder of the discussion, the following notations will be used:

- X_1 = % w/w of starch, USP in powder mixture
- X_2 = % w/w of pregelatinized maize starch in powder mixture
- X_3 = % w/w of talc, USP in powder mixture
- X_4 = % w/w of zinc oxide, USP in powder mixture (% expressed in decimal)

Thus, the powder mixture used at any time may be characterized by the vector $(X_1 X_2 X_3 X_4)$. It will be noted that $X_1 + X_2 + X_3 + X_4 = 1$ and hence if any three quantities are given, the other is redundant. Therefore, X_4 was used as the redundant quantity in the analysis.

The design of the experiment chosen was used in another research

³ Lightnin' No. F.

⁴ P-K Twin-shell Yoke model.

Table I—Combinations of Solids Used for Absorption Studies

Combination	Percent ^a			
	X ₁	X ₂	X ₃	X ₄
1	1.000	—	—	—
2	—	1.000	—	—
3	—	—	1.000	—
4	—	—	—	1.000
5	0.500	0.500	—	—
6	0.500	—	0.500	—
7	0.500	—	—	0.500
8	—	0.500	0.500	—
9	—	0.500	—	0.500
10	—	—	0.500	0.500
11	0.333	0.333	0.333	—
12	0.333	0.333	—	0.333
13	0.333	—	0.333	0.333
14	—	0.333	0.333	0.333
15	0.250	0.250	0.250	0.250
16	0.718	0.094	0.094	0.094
17	0.094	0.718	0.094	0.094
18	0.094	0.094	0.718	0.094
19	0.094	0.094	0.094	0.718

^a X₁, X₂, X₃, X₄ = % w/w starch, pregelatinized maize starch, talc, and zinc oxide, respectively.

project of this type (12). The various combinations of the solids used are shown in Table I.

The first part of the analysis involved data reduction. It was observed that if, for each tensiometer and each combination, the suction force (indicated by rise in mercury column) at time *t* was plotted against the variable *t*/(*t* + 1) on log paper, the plots fell approximately along a straight line. This fact indicated that the following model would apply for the degree of absorption over time *t* for a specific dispersion:

$$X_t = \omega [t/(t + 1)]^\alpha \epsilon_t, t \geq 0 \quad (\text{Eq. 1})$$

where

- X_t = observed rise in mercury column at time *t*
- ω = an unknown parameter which represents the absorptive capacity of the dispersion
- α = an unknown parameter which is related to the rate of absorption
- ε_t = a random uncontrollable error which is nonnegative and has an expected value of unity

If the logarithm of both sides of Eq. 1 is taken, it may be rewritten as:

$$Y_t = \beta + \alpha Z_t + \epsilon_t', t \geq 0 \quad (\text{Eq. 2})$$

where

- Y_t = log X_t
- β = log ω
- Z_t = log (t/(t + 1))
- ε_t' = log ε_t

Equation 2 is the most convenient form for estimating the unknown parameters in Eq. 1. It can be seen that in Eq. 2, Y_t and Z_t are linearly related in accordance with the preliminary graphing discussed above.

Emphasis should be made that β (and consequently ω) and α depend on the combination (X₁ X₂ X₃) which can be designated by β = β(X), α = α(X) where X = (X₁ X₂ X₃). This notation will be used when referring to dependence. Parameter β represents the logarithm of the stationary position of the mercury in the tensiometer and is related to the amount of water absorbed. The assumption was made that it was physically possible for all dispersions to reach a stationary absorption point. The α parameter is related to the rate of change of the mercury in the manometer.

β and α were estimated by the least-squares technique for each combination. The experiments which were run immediately after mixing and those standing for 24 hr. were treated separately at

Table II—Summary of Calculated and Observed Data for Various Combinations of Solids in a Lipophilic Base

Combination	$\hat{\alpha}$	$\hat{\beta}$	S ² (log mbar.)	Manometer Readings at 0.5 hr., mbar.	$\hat{\omega}$, mbar.
	log mbar./log (t/t + 1) (Rate of Change)	log mbar. (Absorptive Capacity)			
1	1.0661	1.8710	0.0428	22.0	74.3
2	0.7830	3.0881	0.0161	513.3	1224.9
3	0.0000	—∞ ^a	0.0000	0.0	0.0
4	0.7986	3.1946	0.0113	665.0	1565.3
5	1.2218	2.9023	0.0518	193.2	798.5
6	6.6750	1.2274	0.0925	0.4	16.9
7	1.6750	1.2505	0.0973	3.2	17.8
8	0.7338	2.1909	0.0212	68.2	155.2
9	0.9636	2.9184	0.0262	278.8	828.7
10	5.0000	0.7124	0.0701	0.0	5.2
11	1.1073	2.4570	0.0454	78.0	286.4
12	1.1353	2.5528	0.0512	94.8	357.1
13	5.3053	1.2936	0.0948	0.0	19.7
14	0.9664	2.4889	0.0348	101.2	308.2
15	1.0060	2.3192	0.0385	64.8	208.5
16	1.0082	1.8868	0.0396	24.8	77.1
17	1.1216	2.9340	0.0488	232.2	859.0
18	0.6001	0.9689	0.0257	4.6	9.3
19	1.2402	2.2553	0.0620	42.6	180.0

^a This combination produced no absorption, and hence Eq. 1 with $\hat{\alpha} = 0.0$ and $\hat{\omega} = 0.0$ perfectly describes the results. This means that $\hat{\beta} = -\infty$.

first to determine if there was an aging effect on the dispersion. By a multivariate analysis, it was concluded that the 24-hr. aging period produced no statistically significant differences in the parameters describing the absorption.

In light of this, the estimates for the initial and 24-hr. periods were pooled to give one estimate of α and β for each combination. These estimates along with the estimates of the residual variation, S², at each combination are given in Table II. The residual variation gives a measure of the scatter of the data about the "fitted" model (Eq. 2). In other words, once α and β are estimated for a given dispersion, by $\hat{\alpha}$ and $\hat{\beta}$, then ignoring the ε_t' in Eq. 2, the fitted model would be:

$$Y_t = \hat{\beta} + \hat{\alpha} Z_t \quad (\text{Eq. 3})$$

Equation 3 may be plotted as a straight line of Y_t against Z_t, and the observed data (in logs) may be plotted on the same graph. The residual variation (Table II) indicates the average distance a data point is from the plotted line. Residual variation is in squared units, i.e. (log mbar.)². The manometer readings of the combinations during the first 0.5 hr. are also shown in Table II. One-half hour was the greatest common observation time for all combinations.

The S²s are not very different, with the exception of combination No. 3, and in this sense, Eq. 2 fits each combination equally well. Combinations 4 and 2 are the first- and second-best mixtures, respectively, based on the $\hat{\beta}$ parameter and the 0.5-hr. absorption period; they do not differ significantly with respect to the $\hat{\alpha}$ parameter.

At this point, absorption properties of the various combinations of powders have been summarized by two parameters, α and β. The experiment can be reconstructed for a given combination if $\hat{\alpha}$ and $\hat{\beta}$ for that combination are known. In order to do this, $\hat{\alpha}$ and $\hat{\beta}$ must be put in Eq. 3 and the equation plotted on arithmetical paper. This reconstructs the log of the absorption as a function of log (t/t+1).

It was then natural to ask if the $\hat{\alpha}$'s and $\hat{\beta}$'s vary in any predictable way with the combination. In other words, can a curve be calculated for a particular combination just from a knowledge of X₁, X₂, X₃? If the answer to this question is yes, an interpolation could be done for various mixtures.

In order to investigate this further, the following quadratic model

for the vector $(\hat{\alpha}, \hat{\beta})$ was considered:

$$\hat{\alpha}(X) = \mu + \sum_{j=1}^3 \gamma_j X_j + \sum_{j=1}^3 \gamma_{jj} X_j^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \gamma_{ij} X_i X_j + \epsilon \quad (\text{Eq. 4})$$

$$\hat{\beta}(X) = \mu' + \sum_{j=1}^3 \gamma_j' X_j + \sum_{j=1}^3 \gamma_{jj}' X_j^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \gamma_{ij}' X_i X_j + \epsilon' \quad (\text{Eq. 5})$$

where

- $\mu(\mu')$ = overall effect of the mixture
- $\gamma_j(\gamma_j')$ = parameter measuring linear dependence on the different powders
- $\gamma_{jj}(\gamma_{jj}')$ = parameter measuring quadratic dependence on the different powders
- $\gamma_{ij}(\gamma_{ij}')$ = parameter measuring the interaction of the powders with one another

All these parameters were unknown and had to be estimated from the data, *i.e.*, observed $\hat{\alpha}$ and $\hat{\beta}$. At this point, effort was made to simplify Eqs. 4 and 5 by eliminating some of the terms. The statistical technique was a multivariate regression analysis and the following conclusions were drawn relative to the simplification:

$$\begin{aligned} \gamma_{11} &= \gamma_{11}' = 0 \\ \gamma_{12} &= \gamma_{23} = \gamma_{12}' = \gamma_{13}' = 0 \end{aligned}$$

With these adjustments made in Eqs. 4 and 5, the simplified model was as follows:

$$\hat{\alpha}(X) = \mu + \sum_{j=1}^3 \gamma_j X_j + \sum_{j=2}^3 \gamma_{jj} X_j^2 + \gamma_{13} X_1 X_3 + \epsilon \quad (\text{Eq. 6})$$

$$\hat{\beta}(X) = \mu' + \sum_{j=1}^3 \gamma_j' X_j + \sum_{j=2}^3 \gamma_{jj}' X_j^2 + \gamma_{13}' X_1 X_3 + \epsilon' \quad (\text{Eq. 7})$$

Equations 6 and 7 were fitted to the data, *i.e.*, the parameters in Eqs. 6 and 7 were estimated, with the following results:

$\hat{\mu}$	=	2.2164	$\hat{\mu}'$	=	2.4351
$\hat{\gamma}_1$	=	-0.7124	$\hat{\gamma}_1'$	=	-0.9571
$\hat{\gamma}_2$	=	-8.1270	$\hat{\gamma}_2'$	=	2.8704
$\hat{\gamma}_3$	=	12.4284	$\hat{\gamma}_3'$	=	-2.6388
$\hat{\gamma}_{22}$	=	6.9547	$\hat{\gamma}_{22}'$	=	-2.2598
$\hat{\gamma}_{33}$	=	-19.4543	$\hat{\gamma}_{33}'$	=	0.0954
$\hat{\gamma}_{13}$	=	9.3716	$\hat{\gamma}_{13}'$	=	2.2662

When these estimated values are put in Eqs. 6 and 7 and ϵ, ϵ' are set equal to zero, prediction equations for $\hat{\alpha}(X)$ and $\hat{\beta}(X)$ in terms of X_1, X_2, X_3 result.

The multiple correlation coefficient R is a measure of how well the fitted model can be used in prediction. In this experiment, there are $\hat{\alpha}$ and $\hat{\beta}$ predictors and there is a corresponding $R_{\hat{\alpha}}$ and $R_{\hat{\beta}}$. R^2 is actually the percent of total variation in the data which can be accounted for by the model. The R^2 values that approach unity indicate good prediction. The following values were calculated: $R^2_{\hat{\alpha}} = 0.80$; $R^2_{\hat{\beta}} = 0.98$. Thus, good results can generally be expected from the $\hat{\beta}$ predictor but probably not from the $\hat{\alpha}$ equation. This equation for $\hat{\beta}$ may be useful in estimating the amount of water (in log mbar.) which would be absorbed by some particular com-

bination of powders studied—whether or not the particular dispersion is tested.

SUMMARY

The absorptive properties of various combinations of starch, USP, pregelatinized maize starch, talc, USP, and zinc oxide, USP dispersed in light liquid petrolatum, NF were investigated. The suction force and mercury rise in the manometer were measured in terms of millibars with the tensiometer.

The performance of these dispersions was evaluated in terms of two estimated parameters, $\hat{\alpha}$ and $\hat{\beta}$. Parameter $\hat{\alpha}$ is related to the absorption rate while $\hat{\beta}$ is related to the absorptive capacity (the theoretical stationary point when equilibrium is attained). It was found that $\hat{\beta}$ varied in a predictable way with the various combinations of powders. This means that $\hat{\beta}$ is quite predictable from a knowledge of proportions of starch, pregelatinized starch, talc, and zinc oxide represented by X_1, X_2, X_3, X_4 , respectively. The $\hat{\alpha}$ apparently does not vary in a predictable manner.

Zinc oxide was found to be the best powder in terms of rate and absorptive capacity, followed by pregelatinized maize starch. Talc is not suitable for use in a lipophilic base such as light liquid petrolatum in regard to absorbing water.

Some interaction among the powders was noted when various ones were mixed together. This was exemplified empirically by noting that when zinc oxide and pregelatinized starch were mixed together, the absorption properties were reduced considerably. Statistically, this was evident in the conclusion that γ_{13} , the parameter measuring the interaction of the powders with one another, was not zero in Eqs. 6 and 7. Both starch and talc interacted when mixed in combinations with each other as well as with the other solids to cause a decrease in water absorption.

There was no significant effect on the absorptive properties of the dispersions by allowing them to stand for 24 hr. The instrumentation and procedure appear to be applicable to the study and evaluation of other solids dispersed in various bases.

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