PREDICTION OF THE RHEOLOGIC AGING OF COSMETIC LOTIONS

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Presented September 20, 1962, Seminar, New York City

In studying the aging of cosmetic lotions after preparation, the cosmetic formulator often finds himself on the horns of a major dilemma: how to predict from short periods of time what will happen during the normally accepted shelf life. The normal rule of the chemist for determining shelf life is to set samples at a series of temperatures and to evaluate a classic rate constant for the reaction. The formulator is beset by the problem that his creations frequently have extremely complex behavior when stored at various elevated temperatures, for example, the classic heat hardening of many soap-containing formulations. In such a case, from the phase rule viewpoint, his formula is simply moving at reasonable rates into the ever present gel regions characteristic of long chain compounds in water. However, at lower temperatures this often never happens, for the rates are so much slower.

Alternately, the elevated temperatures lead to the melting of one or more components and hence a complete change in the nature of the formulation. Often high temperatures maintain an impurity in solution so that the high temperature forms remain satisfactory when those stored at lower temperatures soon become cosmetically unelegant. Thus, though the formulator uses accelerated testing as a guide, he feels forced to rely ultimately on room temperature behavior. Certainly the standard Arrhenius relation seldom is of use to him, and his systems rarely obey conventional kinetics.

The formulator usually uses observing periods of roughly doubled time intervals—thus 1, 2, 4, 7 and 14 days; 1, 3, 6 and 12 months. Experience has taught him that in these time intervals he may expect to see sufficient change to justify the observations. More frequent observation is usually impossible because of the demands on his time.

However, the normal frame of reference is based on the linear time scale; and it is often said that the changes are leveling off. That is, there is an asymptotic approach to a limit, since as much change occurs in going from one to three months as occurred in one to three days.

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Purchased for the exclusive use of nofirst nolast (unknown) From: SCC Media Library & Resource Center (library.scconline.org) Several years ago, as a matter of convenience, one of us (G. C.) began using logarithmic plots as a convenient compacting device to consolidate rheological data from days to months onto a reasonable plot that would give equal weight to all observations. It was soon evident that for many viscosity plots a reasonably good straight line was obtained for a plot of the logarithm of viscosity against logarithm of time, using any suitable units. The first tentative mention of this was over a year ago (1). Since that time, we have sought to examine the possible generalization of such a relationship and the underlying logarithmic time dependency in order to assess the reliability of the generalization and hence in turn the significance of any departure from such a behavior.

Of course, empirical line straightening and data compaction are often obtained by the use of square root or higher roots of the variable. To obtain a crude linearity between a root plot and a logarithmic one, it is necessary to use a root power at least 0.5 greater than the number of logarithmic decades considered. Therefore, for four or more time decades the power root dependency on time is theoretically not probable.

OCCURRENCE OF THE LOGARITHM TIME DEPENDENCY

First it is well to examine how significant is the aging property dependence on logarithm of time, as evidenced from published literature. The examples chosen are not intended to be complete but rather were chosen because they were known to the authors as cases where a logarithmic time dependency was found empirically necessary.

Two examples of emulsion stability were available. The first by Menczel *et al.* (2) clearly demonstrated by a colormetric technique that the logarithm of the per cent separation of internal phase was directly related to the logarithm of time for time periods from minutes to several days. These authors suggested an emulsion stability grading system based on this relationship. A similar relationship was found by Christian (3) for the creaming rates of various emulsions using radio isotopic measurements for the ratio present at the top and the bottom of a cylinder.

We have recently reported (4) that the viscosity build-up by hydration of Veegum[®]*, a bentonite type clay, regardless of the temperature of storage, is related to the age of the suspension by a linear log-viscosity log-time relationship, holding over a time range of hours to months.

In a recent paper, Levy (5) reports the build-up with time of the various rheologic parameters useful to characterizing a bentonite gel, dynamic and static yield value, thixotropic area, and plastic viscosity. As may be seen from Fig. 1, these properties are well characterized when plotted on a log-property log-time plot by a straight line relation.

Chong (6) showed that the growth of anti-thixotropy for a magnesia

^{*} Veegum is a trade name of the R. T. Vanderbilt Co., Inc.

magma was related to the logarithm of time. Subsequently he found (7) that a better linear relation held for a plot of the logarithm of the growth against logarithm of time.

In another recent paper, Levy (8) has studied recovery rates from disturbances in strongly thixotropic bentonite gels. He reported that the recovery strength of the gel was related to the logarithm of time in a manner analogous to that noted by Chong (6). Actually, in the range of recoveries observed by him, the logarithm of recovery would fit the data quite as well and for our purposes may therefore be assumed to hold.

In the field of metallurgy (9), it has long been an empirical fact that many annealing processes are well depicted by the log-log plot against time.

Similarly the exchange reaction of HCl gas on sodium chloride (10) follows this relationship. Other experiments (11) studying irradiation defects have equated a linear function of per cent change to the logarithm of time, while a group (12) studying the polymorphic transition in tin utilized a double log function of the fraction transformed as the variable against the logarithm of time.

THEORETICAL BASIS FOR THE RELATIONSHIP

Avrami (13) has examined the general kinetics of phase transformation in solid systems and has shown that, for conditions of isolated nucleation, a proportionality can exist between transformed volume and a power of the elapsed time. If it is assumed that we are dealing in systems where such isolated nucleation of changes is diffusion inhibited, then thick cosmetic lotions should, in a first approximation, obey this proportionality. If it is then assumed that the extensive property (P) under examination is directly related to the degree of transformation that occurred in time (t), then

$$P = a t^{b}$$

and $\log P = b \log t + c$

where a, b and c are constants of the systems to be evaluated empirically.

For cosmetic lotions, diffusion controlled and isolated nucleation reactions are possible in many cases. Certainly, the diffusion control of the solid state might be expected to be less rigorously obeyed for a viscous semiheterogeneous mixture than for the solid, and indeed this is the general case in the cosmetic lotions. However, the resultant behavior should be expected to be some compromise between the normal kinetics of the homogeneous system which involve a linear function of time and the limiting solid-state type dependency on the logarithm of time.

Application to Cosmetic Lotions

In Fig. 2 are shown logarithmic viscosity-time plots for several different systems. The solid lines represent heat emulsified solid fat systems, the dotted line a hand lotion, and the dashed lines antiperspirant lotion formu-

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Figure 1.—Data of Levy and Rutowski (5) replotted on logarithmic basis, to show the build-up of the rheologic parameters of bentonite with time.



Figure 2.—Some aging curves of cosmetic lotions. (---- cosmetic hand lotion, —— "solidified" fat systems from a hot emulsion, — — antiperspirant lotions).

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Figure 3.—The change in shear stress with time for three different shear rates for an antiperspirant lotion.

lations. In each case, the linearity is quite satisfactory. In this example, we have arbitrarily used the viscosity at one second⁻¹ shear rate as read graphically from a rheogram. Other choices are open, and in Fig. 3, for one lotion, aging curves at three different shear rates are shown for the actual shear stress measurement. It is apparent from these curves that the



Figure 4.—Aging curves for various formulation and process variants of a lotion subject to age hardening.

low shear yield value term is building at a faster rate than the plastic viscosity. Thus a series of lines may summarize for a lotion any desired shear properties.

In some cases, after an initial period of linearity, the slope of the line shows an increase with time (see Figs. 4 and 5). Such an increase is frequently followed by a marked drop. At this time we are inclined when using these plots to consider that as long as the linear holds, regardless of the slope, the lotion or paste is behaving normally. Of course, it is ideal if the aging curve is flat, but this is seldom seen. If a tendency toward



Figure 5.—Effect of delayed filling on the aging viscosity of a lotion. (— — filled the same day as making; — filled the following day.)

marked upward curving becomes apparent after some variable induction period, we consider that excessive "hardening" is possible. This abnormal increase often is the forerunner of an eventual drop in viscosity signifying phase separation.

IMPLICATIONS OF THE USE OF LOG TIME PLOTS

First it is of interest to note that the average time-doubling scale so frequently used for cosmetic lotion observation is close to the logarithm time choice favored here.

Secondly, the logarithmic scale of viscosity has been shown by Fryklöf (14) to be directly related to a linear scale of subjective or ocular judgment of consistency.

What in practice is gained by the logarithm plot of property and time? When there exists a simple and essentially linear relation, and this is reasonably common, there are two major advantages which can be of great value to a stability program. The first is that as long as a reasonably linear relation holds there is considerable confidence that aging is not inducing any unanticipated complications. The other, and possibly the most important, is the tentative long range prediction available from early measurements, especially when anchored by the normally more rapidly changing values of the very early hours after formulation. Usually, because the changes are so rapid in the first one or two days, these observations are often very limited or more commonly completely ignored. We prefer to get several points in this time region, preferably from as early as one-half to one hour after formulation. In this manner we have established the projection of the line through one or more decades of time (in days) without having to wait a week or more to pass. At any time interval, projection to at least double that time is very safe, and frequently several mutiples can be used with discretion. In general we have always utilized the time interval of days in our plot. Thus at two to three days we feel that we can project in a rapidly changing system to ten days. By one hundred days we feel one year's prediction to be quite safe.

Now, unfortunately, the linearity is not always there. There are, of course, only two directions for deviations. If the curves deviate downward, that is, the suspension thins out, then, of course, stability is dubious and it requires no great refinement of data to realize this. If the deviation is upward, then the suspension is thickening at a rate that can only lead to trouble. In the extreme, we have found such cases to be linear with time, and hence the reaction is not diffusion controlled. In such cases the more usual kinetics govern. Such systems often involve hydrolysis of one or more components or the direct reaction between two components. Obviously such reactions are more likely to proceed rapidly in the more fluid systems.

COSMETIC LOTION PROCESS STUDY

The logarithmic plot serves as an excellent tool to compare process variables during an aging investigation. Thus in Fig. 4 are seen a few of the various formulations and process attempts to prepare a lotion of acceptable rheological behavior. It is quite obvious that such a graph clearly permits comparisons between formulations in a manner that no other plot can do because of the range of values involved.

Similarly in Fig. 5 we see the effect of delayed filling on a cosmetic lotion subject to separation. It is striking that the delayed shear effects, so pronounced during the initial aging period of the sample (15), can continue for so long.

In Fig. 6 are seen the effects on one batch of a cosmetic lotion of withdrawing a portion before the temperature had been dropped completely in the finishing step. Both portions were each filled the same day and after one-day's storage. The unfilled and the same-day-fill portions were indistinguishable for both finishing conditions throughout the duration of the study. However, the aging patterns for the two finishing temperatures are quite different. For both samples the effect of delayed fill on rheology was quite pronounced.



Figure 6.—Effect of two finishing temperatures and delayed fill on the rheologic aging of one batch of a lotion. O—higher temperature, unfilled and same day filling; O—higher temperature, filled second day; O—lower temperature, unfilled and same day filling; O—lower temperature, filled second day.

In Fig. 7 are shown a few of the results obtained for a lotion containing triethanolamine. The upper, flat, line represents the use of straight 98% "pure" triethanolamine. The lower, steepest, curve is for 25% of this and 75% of the technical grade. The intermediate curve is for a 50-50 mixture. Straight technical grade material yields a line close to the 50-50 one but slightly lower. The curve for 75% "pure" was intermediate between the 100 and the 50% mixtures. Variants on this formula minimized this difference. As before, the logarithmic plot permits a compacted evaluation of the whole aging pattern.

Effect of Temperature on Aging

In our work (4), a clean-cut dependency of the logarithm of viscosity on the reciprocal of the absolute temperature was noted for the setting up of a Veegum suspension. This is typical of the behavior in a system where rigid kinetics dominate throughout. Similar results are also classic in the metallurgy field.

Figure 8 shows the results of storing a cosmetic lotion at several temperatures for a prolonged period. It is immediately apparent that with increasing temperature other phenomena enter, and there is no continuous relation between property and temperature. Indeed, temperature inversion, as here, is the frequent rule. Often, and probably in this case, one of the other phenomena is melting of one or more of the components of the lotion.

Except in rare cases, we do not find that we can anticipate much in rheologic behavior from accelerating aging. One important exception to this, however, should be noted—upward deviations generally occur much earlier as the temperature is raised, and so the use of the elevated temperature can be a warning of probably eventual similar behavior at room temperature.

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Figure 7.—Aging of a lotion prepared with different ratios of 98% and of technical grade triethanolamine.

It is intended later by the study of the equation of flow to attempt to derive parameters from such equations that will recognize the likelihood of this type of behavior before it is clearly established. Our first efforts in this regard are promising, but considerably more work will be necessary before it can be clearly established.



Figure 8.-Effect of temperature on the aging properties of an antiperspirant formulation,

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SUMMARY

The use of plots of the logarithm of time with the logarithm of the various extensive properties examined in an aging program is suggested as the best way to evaluate the normality of the aging process.

Deviations from linearity may be used as guides in anticipation of untoward behavior.

The linearity of the logarithmic plot of time and extensive property permits safe prediction of properties for two to three age periods beyond the last observation.

Its utilization in the course of process and formulation studies permits a compacting of considerable data for comparison into one or more convenient graphs.

(Received September 18, 1962)

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