

Lubricity of Dilute Solutions of Hydrocolloids

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To determine relative lubricity of hydrocolloids at low viscosities, the friction values of dilute solutions of seven hydrocolloids were measured with the lubrimer. At very low viscosities, hydrocolloids impart no lubricity to water. A certain consistency appears to be a prerequisite for hydrocolloid dispersions to be effective as lubricants, except for a high molecular weight polymer of ethylene oxide.

IN A PREVIOUS paper on lubricity (1) it was shown that, in the case of hydroxypropyl methylcellulose gels, lubricity was not a function of viscosity. Rather, lubricity was directly related to the solid content of the dispersion regardless of the viscosity grade of the methylcellulose. Thus, dispersions of equal concentrations of two hydroxypropyl methylcelluloses¹ had identical lubricity values (but quite different viscosities).

The lubrimer, with which the decrease in friction was measured (2), consists basically of two cylinders separated by a film of lubricant. The lower cylinder is rotated at a constant speed; the upper one, to which a spring is attached, rests on the lower cylinder and its motion is activated by the turning of the lower one. The extent of the rotation of the upper cylinder depends on the friction between the surfaces of the two cylinders. If friction is high, the upper cylinder is pulled along up to half of its circumference thereby stretching the spring until the restoring force of the extended spring equals the pull of the upper cylinder. The extension of the spring is a measure of the friction value, which is expressed in grams. The greater the stretch, the greater the friction, and *vice versa*.

The movements of the two cylinders in the lubrimer facilitate the formation of a converging fluid wedge along the line of nearest approach of the cylinders. This fluid wedge, which is an essential feature of hydrodynamic lubrication, increases the flow velocity of the lubricant and subjects it to great shear, which, in turn, decreases the apparent viscosity of hydrocolloids. Thus the lubricant effect of hydrocolloid gels, all of which have non-Newtonian flow characteristics, may not parallel empirical impressions of lubricity. By rotating the driving cylinder at a slow speed, however, this effect on the viscosity was decreased. Although it was established that lubricity was not simply related to viscosity, at least in the case of methylcellulose, viscosity is, nevertheless, a contributing factor to lubricity. A comparison of different hydrocolloid gels with regard to their lubricity might

well be invalidated by the distortion of viscosities. Since no quantitative expression exists for lubricity of aqueous systems, such as Petroff's equation for friction and lubricity in metal bearings (3), the contribution of viscosity to the lowering of friction remains shrouded.

Very dilute solutions of hydrocolloids have low viscosities and they approach, furthermore, Newtonian flow characteristics as the concentration of hydrocolloid decreases. The effect of viscosity on the measurement of lubricity in such dilute solutions would be minimal. In addition to the fundamental aspects of such a study, practical applications are also conceivable. Although medicinal lubricants are usually of gel consistency, mobile solutions, as used for irrigations, enemas, and lotions, can be improved by the addition of a water-soluble lubricant.

Among the several hydrocolloids which were studied were representatives of the natural plant gums, semisynthetic cellulose ethers, and totally synthetic products. Where several viscosity grades of a product existed, a low viscosity type was selected. Except for one hydrocolloid, only solutions with viscosities of less than 1000 cps. were incorporated in the study.

EXPERIMENTAL

Materials—Commercially available hydrocolloids were used except for a polyethylene glycol resin of very high molecular weight² and hydroxyethyl cellulose,³ samples of which had been furnished by their manufacturers. Naturally occurring hydrocolloids were represented by nonionic guar gum⁴ and anionic carrageenin.⁵ Three cellulose derivatives were used: nonionic hydroxypropyl methylcellulose,⁶ anionic sodium carboxymethylcellulose,⁷ and nonionic hydroxyethylcellulose.³ Representatives of the synthetic hydrocolloids were anionic neutralized carboxy vinyl polymer⁸ and nonionic polyethylene glycol resin.²

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¹ Methocel 90 HG 400 and Methocel 90 HG 4000. Dow Chemical Co., Midland, Mich.

² Polyox WSR 301. Union Carbide Corp., New York, N. Y.

³ Natrosol, low viscosity type. Hercules Powder Co., Wilmington, Del.

⁴ JaGuar A-20-D. Stein Hall and Co., New York, N. Y.

⁵ Viscarin, standard grade. Marine Colloids, Springfield, N. J.

⁶ Methocel 90 HG 400. Dow Chemical Co., Midland, Mich.

⁷ Cellulose Gum 7 L. Hercules Powder Co., Wilmington, Del.

⁸ Carbolip 934. B. F. Goodrich Chemical Co., Cleveland, Ohio.

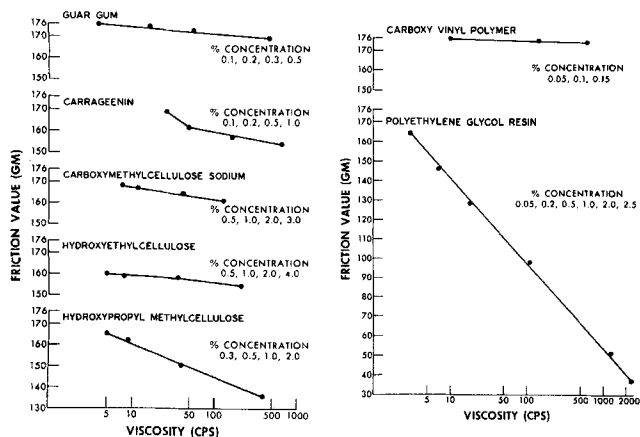


Fig. 1—The effect of hydrocolloid concentration on lubricity and viscosity.

Apparatus and Procedure—The lubrimeter and its use were described previously (2). A single spring was used which covered the whole range of lubricities examined. Its total range was somewhat less than the range of lubricities covered with several springs and, therefore, the difference between extremes of high and low friction was less than in previous experiments. Thus water had a friction value of 176 Gm. as compared with previous readings of 203 and 210 Gm., respectively. Glycerin gave a reading of 29 Gm. (previously 22.7 Gm.). All measurements were carried out at room temperature, which fluctuated between 21° and 24°. Otherwise, the same procedure was followed as described previously.

Viscosity determinations were made with the Brookfield viscometer, model LVF, at temperatures of $22 \pm 1^\circ$ and spindles No. 1 and No. 3. Each hydrocolloid solution was measured at speeds of 6, 12, and 30 r.p.m. and the scale readings were converted to cps. Up to about 500 cps. differences in apparent viscosities, if any, were small. The viscosities used for the purpose of comparison were based on the scale readings at 12 r.p.m. At very low viscosities (up to about 8 cps.) the instrument's readings were erratic; such low viscosity values may, therefore, be inaccurate.

RESULTS AND DISCUSSION

Figure 1 illustrates the results for each of the hydrocolloids examined. All but one exhibit little or no lubricity. This was not unexpected since in aqueous systems generally only full fluid or hydrodynamic lubrication is effective. This type of lubrication requires a substantial layer of lubricant between the opposing surfaces which remains in place by virtue of its viscosity. It could not be taken for granted that the lubrimeter, which was designed to measure hydrodynamic lubrication in aqueous systems as applied in a physiological environment was capable of measuring also lubricity when viscosity, a basic condition of hydrodynamic lubrication, was practically absent or very low.

The friction value of water, 176 Gm., was used as the upper limit. Actually, water itself has a lubricating effect, but the addition to it of any hydrocolloid could only lower its friction value. Very low concentrations of a hydrocolloid, as in the

case of the carboxy vinyl polymer, have no effect whatever on the friction value. Even at a viscosity of more than 2000 cps. for a 0.2% solution of this neutralized hydrocolloid—not included in Fig. 1—the friction value was only slightly less than that for the 0.05% solution. A higher concentration of solute, in general, produced a reduction in friction, which was in line with the conclusion of a previous report (1) that the solid content of the solution has a direct bearing on the friction reducing effect. Yet when compared with a known lubricant, such as glycerin, even 3% of one of the hydrocolloids in solution, carboxymethylcellulose, produced no significant lubrication. Its 3% solution had only slightly less friction value than a 0.5% solution. Guar gum, which forms much more viscous systems than carboxymethylcellulose at equal concentrations, had about the same friction value at 0.5% concentration as carboxymethylcellulose. Some of the hydrocolloids had, at low concentrations, a slight effect on the lubricity of their aqueous solutions, others practically none. Only hydroxypropyl methylcellulose, aside from polyethylene glycol resin, improved the lubricity of water at low concentrations and low viscosities.

It was, therefore, surprising to observe a very marked lubricity in polyethylene glycol resin in concentrations comparable to those of other hydrocolloids. At a concentration of 0.5%, the friction value of this resin was already lower than that of any other hydrocolloid tested regardless of concentration. And the slope representing the decrease in friction value with increasing viscosity was considerably steeper than that for methylcellulose, which showed somewhat better lubricity than any of the other five hydrocolloids. Extending the measurements of polyethylene glycol resin to still higher concentrations resulted in a continuing increase of lubricity. Viscosity increased proportionally with the increase of lubricity. At the highest concentration tested, the consistency approached that of a thin gel which was non-Newtonian. Nevertheless, the slope remained the same. However, there was no corresponding further change in lubricity when the concentration was increased beyond 2.5%, only a marked change in viscosity (not indicated on the graph.) The friction value of a 2.5% solution of polyethylene glycol resin was almost as low as that of 95% glycerin (29 Gm.).

The extraordinary reduction of friction by low concentrations of polyethylene glycol resin in water begs an explanation. Aqueous solutions of this resin are non-Newtonian; their apparent viscosities decrease with increasing shear except at very low concentrations. Other liquids having consistencies similar to those of polyethylene glycol resin solutions such as glycerin, or polyethylene glycol of low molecular weight, have also very low friction values. It is worth noting that of three polyols previously measured (1), polyethylene glycol had the lowest friction value and even at a dilution of one part with four parts of water, it raised the lubricity of water significantly.

Hydrodynamic lubrication depends on the inherent viscosity of the lubricant. With decreasing viscosity, hydrodynamic lubrication changes to boundary lubrication, in which a very thin film of only a few layers of the lubricant molecules may separate the surfaces. Solutions and gels of polyethylene glycol resin are apparently effective lubricants at any concentration. It is suggestive to attribute the striking lubricating effect to the linearity and the size of the resin macromolecules; among the most effective lubricants in engineering are linear hydrocarbons (4). At low viscosities, partial hydrodynamic and boundary lubrication coexist because no liquid wedge can be sustained under the pressure of opposing surfaces. If the lubricant film is only a few molecules thick, it must strongly adhere to one or both surfaces or it will be worn away. Solutions of polyethylene glycol resin are very slippery to the touch and stretch fiber-like when being removed from the main body of the liquid. This resistance to being pulled apart is defined as tack (5). The cohesiveness together with adhesion to opposing surfaces distinguish polyethylene glycol resin from the other hydrocolloids and may be partly responsible for its lubricity even in low concentrations. Measurements of adhesiveness of hydrocolloids, with a tackmeter (5, 6) may well contribute to further elucidation of the nature of lubrication with hydrocolloids.

The relationship between friction value and viscosity appears to be linear in the semilog graph.

However, a mathematical analysis was not attempted because of too many variables inherent in the lubrimeter. Although the elasticity of various springs could readily be calibrated, friction values of the same lubricant obtained with different springs but identical plastic sheets and by the same operator were different. The plastic sheets, with which one cylinder of the lubrimeter was covered, gave different results, which necessitated averaging a minimum of 6 measurements. The deviations from the average were always less than 5% and were largest at low friction values. Sheets cut from a different piece of the same type of ribbed polyethylene did not match previous results. Nevertheless, the instrument is capable of comparing quantitatively friction values under carefully controlled conditions.

It is of historical interest that the first instrument to measure the "sliding ability" of pharmaceutical preparations was described more than 30 years ago in the *Journal of the American Pharmaceutical Association* (7); an improved version was described more recently (8).

SUMMARY

The lubricity of several dilute solutions of hydrocolloids was measured with the lubrimeter.

Only a high molecular weight polyethylene glycol resin reduced the friction values of water markedly.

The experimental results were discussed and evaluated.

REFERENCES

- (1) Levy, G., and Schwarz, T. W., *J. Am. Pharm. Assoc., Sci. Ed.*, **49**, 504(1960).
- (2) *Ibid.*, **46**, 558(1957).
- (3) Fuller, D. D., "Theory and Practice of Lubrication for Engineers," John Wiley & Sons, Inc., New York, N. Y., 1956, p. 12.
- (4) Bowden, F. P., and Tabor, D., "Friction and Lubrication," Methuen & Co., London, England, 1956, pp. 97, 107-108.
- (5) Green, H., "Industrial Rheology and Rheological Structures," John Wiley & Sons, Inc., New York, N. Y., 1949, pp. 113 ff.
- (6) Wood, J. H., and Lapham, E. A., *J. Pharm. Sci.*, **53**, 825(1964).
- (7) Lloyd, J. U., Ostwald, W., and Erbring, H., *J. Am. Pharm. Assoc.*, **25**, 386(1936).
- (8) Füller, W., and Münzel, K., *Pharm. Acta Helv.*, **34**, 246(1959).