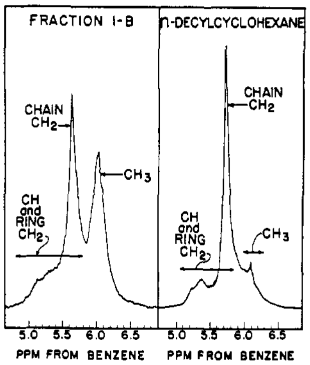

←
Figure 9. Nuclear magnetic resonance spectra for Fractions 1B and for *n*-decylcyclohexane.

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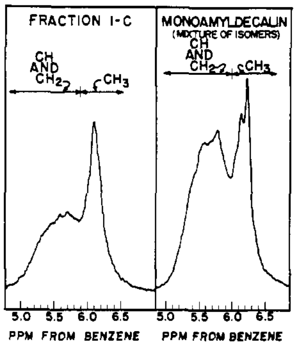
Figure 10. Nuclear magnetic resonance spectra for Fraction 1C and for a mixture of monoamyldecalins.



is a need for spectral data on individual cycloparaffins which have a high proportion of short chains attached to the ring system.

ACKNOWLEDGMENT

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Nitroglycerine Migration in Ethylcellulose

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A STUDY has been made of the effect of changing ethoxy content of ethylcellulose on the migration of nitroglycerin from a standard double-base propellant containing as the volatile constituents nitrogylcerine and diethyl phthalate. Migration decreased in samples having either higher or lower ethoxy content than the usual commercially available materials. Since some of these ethylcelluloses are more difficult to work, as they require high temperatures, they were plasticized to various degrees. The effect of this plasticization on the migration of nitroglycerine was also investigated.

Each anhydroglucose unit in cellulose has three hydroxy groups, any or all of which may react to form derivatives of various degrees of substitution. In the formation of ethylcellulose from alkali cellulose and ethyl chloride complete substitution would give a material containing 54.88% ethoxy. This polymer is known to be weak and brittle and to be a nonthermoplastic having very limited solubility.

An ethylcellulose having approximately 54% ethoxy content picked up no discernible quantity of nitroglycerine. A polymer was desired which picked up very little (ideally no) nitroglycerine, was easily available and capable of being worked, and had acceptable physical properties.

EXPERIMENTAL

Materials. The Dow Chemical Co., Midland, Mich. and the Hercules Powder Co., Wilmington, Del. supplied ethylcellulose samples covering a wide range of degree of substitution. It was found that reproducible results could be obtained using a double-base propellant as the nitroglycerine source. This method, which is safer than using pure nitroglycerine, was applied to all experiments reported here. The propellant, which contained only diethyl phthalate and nitroglycerine as the volatile constituents, was pressed into a billet and subsequently turned into shavings on a lathe to provide a large surface area. 1,1,4,4-Tetramethylbutylphenylether (P-1099) was supplied by the Dow Chemical Co.

Sample Preparation. For initial migration studies a 10% solution of ethylcellulose in toluene or 80% toluene-20% ethanol (more toluene was needed with increasing ethoxy content of the ethylcellulose) was poured within a stainless steel retaining ring floating on mercury. This system was confined in a vacuum desiccator. By placing a piece of filter paper of diameter as large as the desiccator between the body and its lid, the rate of solvent evaporation was easily controlled by applying a slight suction. After the solvent had evaporated, the films were placed in a vacuum oven at 70° C. for 2 days.

For the preparation of the plasticized ethylcellulose samples, flake and plasticizer were mixed at room temperature in a sigma-blade mixer to form a granular feed which was extruded into strands and then chopped. This chopped feed was extruded into sheets, samples of which were machined to the desired thickness (5 to 10 mils) for the migration studies. The same feed was used to extrude a 1-inch rod which was machined into Rossi Peakes samples for softening point determinations. ASTM operating procedure D 569-49, Method A, run at 300 rather than 1500 p.s.i. was used to measure flow properties of these samples.

Migration Studies. A thin, weighed, film of the plastic was placed in a test tube containing a weight of propellant turnings equal to ten times that of the film. This tube was then evacuated for 1 hour (either alone or in manifold with others) by a pump capable of reducing the pressure to 1 micron or below; then sealed off. After a fixed time of storage completely immersed in a thermostated oil bath, the tube was removed and the vacuum released at once. The propellant and the film were reweighed and the plastic film was analyzed polarographically for nitroglycerin content.

It was found expedient to place the solids close together in an evacuated system. Under these conditions, plasticizers exchange rapidly between the materials by a process of isothermal distillation. Since the slow element of the process was diffusion in the solid state, it was possible to speed up the exchange by providing both materials with a large surface area using thin films and shavings.

In the absence of other gases, plasticizers having a vapor pressure of 1 micron or more in the pure state will transfer at a sufficient rate. Thermodynamic principles require that equilibrium exchange be the same with vacuum contact as that which ultimately would be attained with physical contact. Under the conditions of the experiment there were many possible sources of foreign gases within the system itself, even though it was reduced to a low pressure initially—e.g., decomposition of the nitrate esters, dissolved atmospheric gases in the samples, and gases from the glass walls. Since the rates of isothermal distillation of the low vapor-pressure plasticizers are greatly affected by the foreign gas pressure, the results must be considered as qualitative.

Some plastics will continuously absorb nitroglycerine, finally dissolving the plastic completely. Ethylcellulose has much less tendency to absorb nitroglycerine than many other celluloses, for example, cellulose acetate, but depending upon the degree of substitution some could either dissolve or absorb nitroclycerine until some equilibrium value was reached. The arbitrary choice of a 10 to 1 ratio of propellant shavings weight to film weight was calculated to ensure that sufficient nitroglycerine was present to reach or approach the equilibrium concentration, or to dissolve the film. Kinetic experiments have proved that an equilibrium concentration is indeed reached at constant temperature (unpublished results).

RESULTS

Migration Studies. Six thin films of ethylcellulose with ethoxy contents ranging from approximately 45 to 52% were evaluated in duplicate experiments.

Figure 1 illustrates the percentage of nitroglycerine picked up by these samples after 30 and 56 days at a constant temperature of 40° C. Duplicate samples were run for both periods of time and the average of each two identical specimens was plotted. However, no duplicates varied by more than 0.7%.

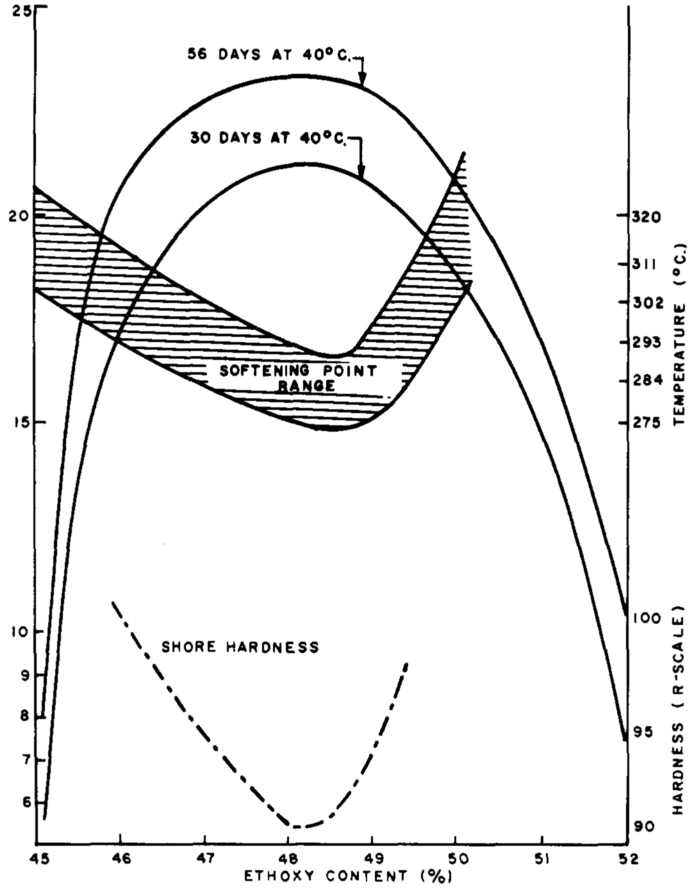

Figure 1. Effect of degree of substitution of ethylcellulose on nitroglycerin migration, softening range, and Shore hardness

Included in Figure 1 are curves showing the effect of ethoxy content on approximate softening range and on Shore hardness. Equilibrium pickup at 40° C. may not have been reached; however, the qualitative shape of the final curve would probably not differ very much from those illustrated in Figure 1.

Commercial ethyl celluloses contain between 2.25 and 2.58 ethoxy groups per glucose unit. This corresponds to an ethoxy range of between 45 and 49.5%. An acceptable balance of properties is found within this range. Thus the limits represent materials having the widest field of commercial usefulness.

The possibility of achieving desirable nitroglycerine resistance with acceptable softening range was explored by blending and by plasticization of the most nitroglycerine resistant commercially available ethylcellulose. It was felt that plasticizer effects would be similar in lower ethoxy content materials. The results of this study are presented in Table I.

Table I. Plasticizer Migration After 56 Days at 40° C.

Ethylcellulose, % Ethoxy	P-1099, Wt. %	Nitroglycerine Gain, Wt. %
45/48.5[a]	15	19.8
48.5	20	24.6
45[b]	15	18.7
45	20	23.2
45	30	24.6

[a] 1:1 Mixture of 45% and 48.5% ethoxy ethyl celluloses. [b] Material represents from 44.5 to 45.5% ethoxy.

The 45 and 48.5% ethoxy materials were also blended for melting point studies. Figure 2 illustrates the effect of P-1099 plasticizer content on the softening point of various blends.

DISCUSSION

The experimental solid curves of Figure 1 show maximum gain in nitroglycerine in polymer samples which have an ethoxy content of approximately 48%. This is the region of lowest softening point, lowest Shore hardness, and greatest solubility and compatibility with resins and plasticizers.

One reason for the large crystallinity of cellulose is the large number of hydroxy groups which are available for hydrogen bonding. The forces between molecules are so great that the material decomposes before it melts. As the molecule is substituted, in this case by etheration, not only is the number of hydroxy groups decreased, but also the bulky ethoxy group prevents a close approach of neighboring molecules, effectively creating more disorder or less crystallinity. As the degree of substitution increases, the amount of disorder increases until a limit is reached. Approximately 1.5 to 2.0 ethoxy groups per glucose unit must be substituted before solubility in organic liquids is possible. The predominance of ethyl ether groups over remaining hydroxy groups promotes solubility in solvents which resemble the ether. Alcohol-hydrocarbon mixtures are the preferred solvents for commercial ethyl cellulose. The mixtures require less and less alcohol as the number of hydroxy groups diminish. Triethylcellulose, for example, is dispersible in toluene. The limit of disorder is reached at approximately 48.5% ethoxy ethylcellulose, where there are approximately 2.51 ethoxy groups per glucose unit.

The large crystallinity in the higher hydroxy content materials slows down the penetration of nitroglycerine. and provides fewer sites for it to solvate. In the fully substituted ethyl cellulose there are no hydroxy groups to take part in hydrogen bonding, but there is some sort of order. Each anhydroglucose unit contains the same number of ethoxy groups and their positions are periodically repeated on a rather rigid cellulose backbone. The bulky groups, moreover, hinder free rotation. The material is high-melting and rather brittle. The chemical nature of these ethoxy substituents favors solubility in nonpolar solvents but polar solvents are ineffective and nitroglycerine has difficulty permeating and solvating the polymer. As the amount of substitution is decreased, order decreases, melting point, and hardness decrease, and solubility in a larger range of solvents prevails. Nitroglycerine pickup increases and continues to increase until the number of hydroxy groups reaches a point where there are so many hydrogen bonding sites that crystallinity is increasing and nitroglycerine pickup is again decreasing.

Because of the high temperature required for working lower ethoxy materials, it cannot be safely used, while hot, to contact nitroglycerine or other nitrate ester-containing materials. In an attempt to lower softening temperature while still maintaining a high nitroglycerine resistance, the effect of softening point or range was studied for mixtures of high and low substituted polymers with varying quantities of P-1099 (Fig. 2). The highest curve represents a pure sample of the 44.5 to 45.5% ethoxy material; the lowest, the pure 48.5% ethoxy sample; the curves in between, mixtures of the two.

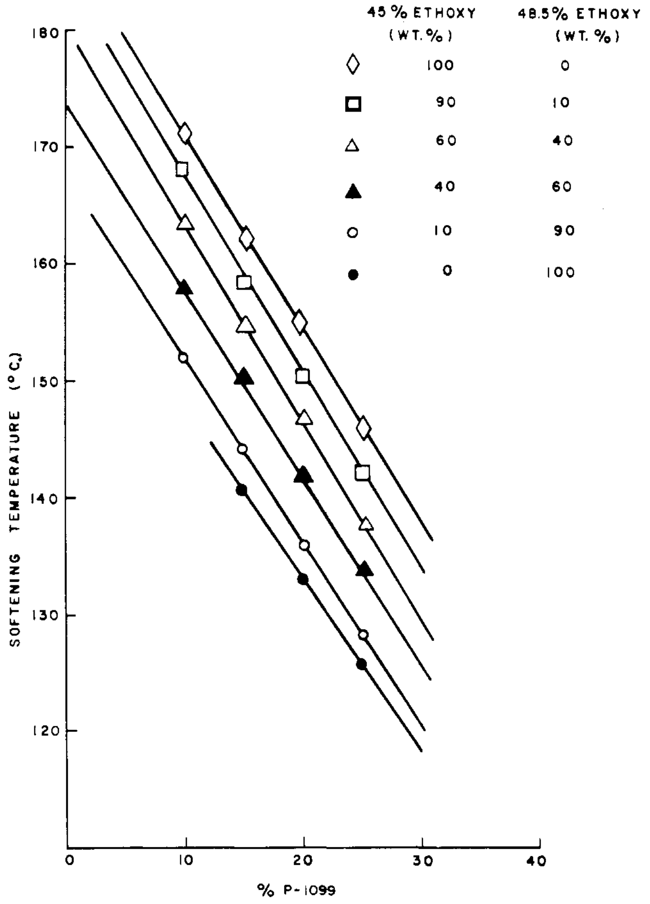

Figure 2. Effect of degree of substitution of ethylcellulose and plasticizer content on softening temperature

The greater the percentage of 45% substituted ethylcellulose the lower the nitroglycerine pickup; however, the temperature required for extrusion increases. Increasing the quantity of the plasticizer decreases the temperature needed for extrustion and increases the amount of disorder. Unfortunately, this increased disorder, or loosening of the chains, also facilitates the entrance of small molecules and the quantity of nitroglycerine picked up is permitted to increase more rapidly.

This experimental work on the effect of per cent ethoxy ethylcellulose on the pickup of nitroglycerine is in agreement with the present picture of the effect of polymer crystallinity and order on the diffusion and solvation by smaller molecules.

CONCLUSIONS

The nitroglycerine affinity of ethylcellulose can be reduced to almost any desired degree by controlling the degree of ethylation. Although pure ethylcelluloses containing lower or higher ethoxy contents than 48.5% may have very little affinity for nitroglycerine, the necessity for adding P-1099 plasticizer to improve workability is detrimental. If no nitroglycerine pickup is to be tolerated, the system described is unsuitable; moreover, the approach employed to meet this objective is impracticable.

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