GRAVIMETRIC DETERMINATION OF MONOLAYER GLYCEROL COMPLEXES OF CLAY MINERALS

By

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ABSTRACT

Glycerol-treated montmorillonite gradually loses one layer of the normal two-layer glycerol complex upon moderate heating at 110°C, forming a monolayer complex with a sharp x-ray diffraction peak at about 14A. In the presence of free glycerol vapor, this complex is quantitatively stable on further heating. A simple gravimetric procedure has been devised to determine the weight of glycerol retained. The procedure involves addition of a dilute glycerol solution to a dried and weighed sample of clay in an aluminum foil dish, and subsequent oven drying over a glycerol surface until constant weight is attained. The portion of the glycerol retained on external surfaces is assessed by measuring the retention of a replicate sample previously collapsed irreversibly by heating at 600°C or higher.

The retention of monolayer glycerol complexes of vermiculite and endellite can be similarly determined. Ethylene glycol forms an analogous series of complexes, and its retention against heating can be measured in exactly the same way. Differential thermal analysis of glycerol- and glycol-treated montmorillonite suggests that both complexes decompose with endothermic reactions at about 300°C.

Glycerol retention values were shown to be independent of sample size and to be almost independent of equilibration temperature between 70°C and 150°C. As expected, they are inversely proportional to particle size. Cation saturation affects the values of both internal and external retention for montmorillonites. It is shown that retention is a function of montmorillonite content in a series of artificial mixtures. Glycerol retention values of a number of clay materials are presented.

INTRODUCTION

In 1950 Dyal and Hendricks introduced a method for the determination of a quantity called the "glycol retention value" of a clay. Glycol retained on external surfaces was estimated by heating replicate samples to 600°C to collapse irreversibly the "expanding" lattice before the addition of glycol. Internal adsorption was considered as the difference between the value obtained for a sample preheated to 600°C and that for a sample dried over P_2O_5. In a later paper Dyal and Hendricks (1952) presented x-ray diffraction data for the glycol complexes of a Wyoming bentonite saturated with various cations, showing the expected x-ray maxima at 17.1A characteristic of a two-molecular layer complex for saturation with H^+, Ca^{2+} and La^{3+}, but more diffuse maxima at lower spacings for saturation with K^+, NH_4^+, Rb^+, and Cs^+.

Kunze (1955) reported that the two-layer glycol complexes of some montmorillonites were not completely stable in air, but appeared to break down after relatively short periods of standing, and to yield diffraction maxima at values well below the expected 17.1A. Considering this apparent lack of stability of the two-layer glycol complex in air, considerable doubt must be raised as to its stability under the conditions of high vacuum specified by Dyal and Hendricks (1950).

Most of the difficulties of the original procedure were remedied by modifications proposed by Martin (1955), who suggested reducing the sample size and including a source of free glycol vapor in the system during the vacuum treatment. The modifications apparently permitted a true equilibrium to be attained rapidly.

MacEwan (1946) has reported that the two-molecular layer complex of glycerol and montmorillonite is stable even in an evacuated camera. Since the vapor pressure of glycerol is considerably lower than that of glycol, it occurred to the present authors that a glycerol complex might lend itself to more reliable measurement of retention and that heating, rather than evacuation, might be employed for removal of the excess glycerol. Several tests were made using thin films of montmorillonites prepared as oriented aggregates by centrifuging the clays on flat porous tiles (Kinter and Diamond, 1956) and, later, on flat strips of heavy aluminum foil. The oriented-aggregate specimens were dried at 110°C, an excess of glycerol was added directly to the clay films, and excess glycerol was removed by heating at 110°C. Using this procedure, it was possible to determine (1) a weight-loss curve by periodically removing specimens from the oven and weighing them, and (2) progressive changes in the condition of the complex by obtaining x-ray patterns immediately after each weighing. This procedure was facilitated by the use of the aluminum strip specimens, which could be cooled to room temperature in about 30 seconds after removal from the oven and weighed before any appreciable amount of water had been adsorbed from the atmosphere.

In general, the data indicated that excess glycerol was removed fairly rapidly with the appearance first of a sharpened 17.7A maximum, and then of a 14A maximum characteristic of a monolayer complex. With further heating, this maximum persisted for a considerable period, but finally broadened and shifted slightly toward the high-angle side, indicating the gradual destruction of the monolayer complex.

In an attempt to obtain conditions more favorable to the stability of the glycerol complex, a source of free glycerol was placed in the drying oven. After a few hours of heating, a definite equilibrium or cessation of weight loss took place, and the 14A peak attained its maximum intensity and sharpness, remaining unchanged with further heating. Figure 1 presents diffraction patterns of a montmorillonite (R-51) at three stages: the two-layer complex; the monolayer complex; and oven-dry, without glycerol. Although the data clearly indicate that at the equilibrium condition the complex corresponds to an extremely regular monolayer arrangement of molecules on the interlayer surfaces of the montmorillonite, no information is given as to the configuration of molecules on external surfaces. However, in a concurrent paper (Diamond and Kinter, 1958), it is shown that the assumption of a monolayer of glycerol on external surfaces of various clay minerals leads to calculations of

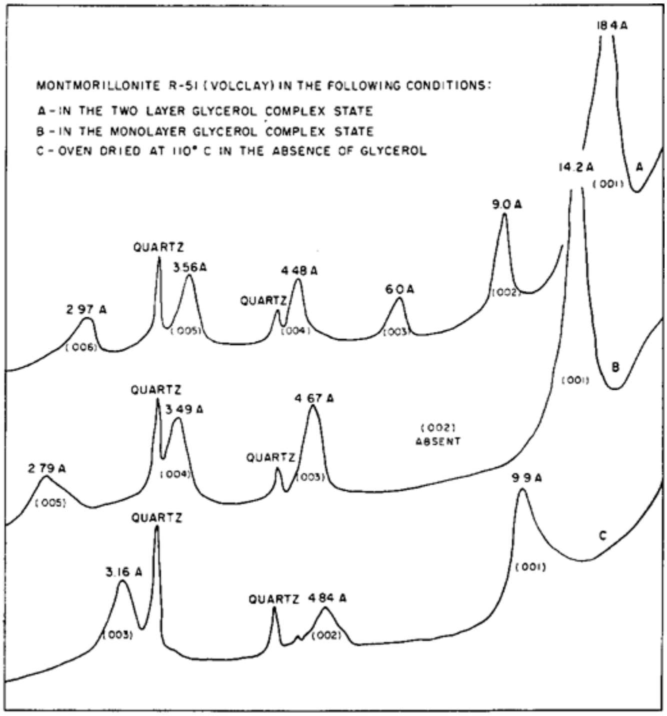

FIGURE 1. — Smoothed tracings of x-ray diffraction patterns of oriented aggregate specimens of montmorillonite (R-51 Volclay).

external surface area which are in good agreement with the results of other methods of surface-area determination.

The state of equilibrium of the montmorillonite monolayer complex is illustrated by the upper curve of Figure 2. Equilibrium was reached in a few hours of heating, and further heating for almost 200 hours failed to bring about any additional loss in weight. The time to reach equilibrium varies with the amount of excess glycerol used. The lower two curves show that weight equilibrium is also reached by illite and kaolinite, which retain glycerol only on external surfaces.

MATERIALS AND METHODS

A simplified experimental procedure suitable for routine determination of glycerol retention at the equilibrium characteristic of monolayer glycerol complexes was developed. Approximately 0.2 g of clay, air-dried and pulverized to pass a 200-mesh sieve, is placed in a weighed aluminum foil dish (Arthur H. Thomas Co. no. 4537, or equivalent), dried at 110°C to constant weight in

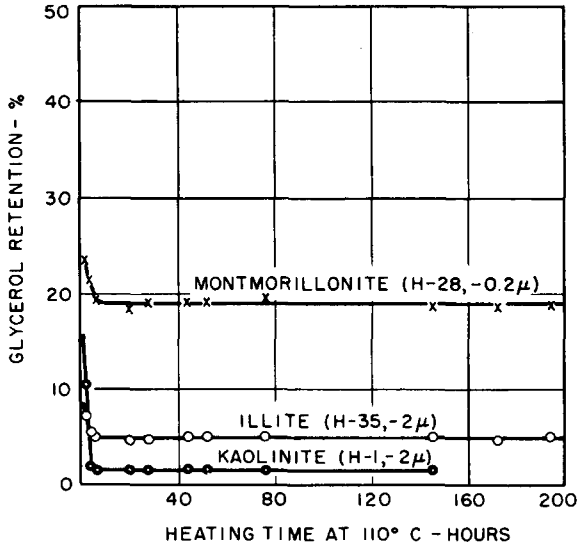

FIGURE 2. — Weight-loss curves for glycerol retention specimens of typical clay minerals.

about 2 hours, cooled in air for 30 seconds, and weighed within the next 30 seconds on an analytical balance preset to the approximate weight. Five ml of glycerol solution (2 percent, in distilled water) is transferred to the dish from a pipette, and the dish is swirled gently to mix and to distribute the mixture evenly. Care must be taken that no unwetted portions of the clay remain. The specimen is then placed in an oven containing a source of free glycerol and heated at 110°C to constant weight. At the condition of constant weight, glycerol retention is calculated as a percentage of the original oven-dry weight of the clay. All weighings are made to 0.1 mg.

Determinations are normally made in duplicate, using glycerol of reagent grade. A blank is included with each group of specimens. The aluminum foil dish is effective and convenient because the clay forms a thin film on the flat bottom and can be removed with pressure-sensitive tape or trimmed to size with scissors and used as a specimen for x-ray diffraction. Upon removal from the oven, the dish and contents cool almost immediately to room temperature, enabling weighings to be made quickly with only negligible adsorption of moisture from the atmosphere. The initial drying and the removal of excess glycerol were performed in separate mechanical convection ovens having heating elements protected from direct contact with the glycerol vapor. Temperatures were controlled to 110°C, ± about 1°C. All x-ray diffraction patterns were obtained with a direct-recording General Electric x-ray diffraction apparatus, with nickel-filtered CuKα radiation. The various clays used in this investigation are described in Table 1.

TABLE 1. — DESCRIPTION OF MATERIALS

Type of Material and Sample No.		Source
Montmorillonite	H-19[1]	Polkville, Mississippi
	H-23	Chambers, Arizona
	H-24	Otay, California
	H-25	Upton, Wyoming
	H-28	Little Rock, Arkansas
	R-51	Wyoming Bentonite (Volclay) American Colloid Co.
Nontronite:	H-33a	Garfield, Washington
Illite:	H-35	Fithian, Illinois
	H-36	Morris, Illinois
Kaolinite:	H-1	Murfreesboro, Arkansas
	H-4	Macon, Georgia
	H-5	Bath, So. Carolina
	R-1	Eng. China Clay "Supreme" Eng. China Clay Sales Corp.
Halloysite:	H-12b	Bedford, Indiana
	H-13	Eureka, Utah
Endellite:	R-137	Chattooga Co., Georgia
Vermiculite:	R-133	Laurens Co., So. Carolina
Allophane (Ando Soil):	S-60	Japan, (U.S.D.A. No. 52936)[2]
Quartz:	R-65	Silica Flour, Ottawa Silica Co.

[1] H-19, etc., are reference clay mineral samples of the American Petroleum Institute series.
[2] Sample furnished by Dr. Lynn Whittig, U.S. Dept. of Agriculture.

EXPERIMENTAL RESULTS

Glycerol Retention by Montmorillonites

The glycerol retention values of several montmorillonites and a nontronite are shown in Table 2, including results both for no pretreatment except drying at 110°C ("total" retention) and for pretreatment at 600°C ("external" retention). Minus 0.2-micron fractions prepared by dispersing the original clays with sodium metaphosphate were used. This preparation implies that in all samples the predominant cation was Na^+, the original cations being retained to an unknown degree. The "total" retention values range from 18 to about 22 percent for the montmorillonites and somewhat lower for the nontronite. Differences in retention among the samples may be the result either of dilution by impurities not detected by x-ray diffraction, or of inherent differences among the montmorillonites, including possible effects of differences in cation saturation. The data in Table 2 also indicate the much lower values of "external" retention obtained after preheating the montmorillonites at 600°C, except for H-25 and H-28, which retained 11.0 percent and 11.4 percent. However, from x-ray diffraction data it was clear that these two had not been collapsed irreversibly by the heat treatment, and their high retention values resulted largely from their remaining ability to expand after heating.

TABLE 2. — RETENTION OF GLYCEROL BY REFERENCE MONTMORILLONITES; MINUS 0.2-MICRON FRACTIONS, Na^+ PREDOMINANT CATION

Sample No.	Total Glycerol Retention[1] Percent	External Glycerol Retention[2] Percent
H-19	19.3	1.8
H-23	18.9	0.9
H-24	22.2	2.0
H-25	18.1	11.0[3]
H-28	18.4	11.4[3]
H-33a (nontronite)	14.2	1.4

[1] Samples dried at 110°C before determination of retention.
[2] Samples heated at 600°C before determination of retention.
[3] X-ray diffraction patterns showed partial reexpansion with glycerol.

Effect of Cation Saturation

The effect of cation saturation on glycerol retention was investigated in an experiment with the R-51 montmorillonite, Volclay. This material was used as received, in the form of a powder passing the 200-mesh sieve, without fractionation or other purification; x-ray diffraction evidence indicated some crystalline impurity, principally about 10 percent of quartz. Homocationic forms were obtained by dispersing the clay in water and treating separate portions of the suspension with appropriately saturated cation-exchange resin (Amberlite 1R-120, Rohm & Haas Co.). As shown in Table 3, values of "total" retention range from 10 percent for K^+ saturation to 17.5 percent for Al^{3+}, the

TABLE 3. — EFFECT OF CATION SATURATION ON RETENTION OF GLYCEROL BY MONTMORILLONITE (R-51, VOLCLAY), WHOLE MATERIAL PASSING 200-MESH SIEVE

Saturating Cation	"Total" Retention[1] Percent	"External" Retention[2] Percent
Na^+	13.9	6.6
H^+	14.5	4.2
Li^+	15.6	3.7
K^+	10.0	2.5
NH_4^+	11.4	4.5
Ca^{2+}	14.0	2.8
Mg^{2+}	16.4	2.0
Fe^{2+}	14.5	2.7
Fe^{3+}	16.0	2.8
Al^{3+}	17.5	2.8

[1] Samples dried at 110°C before determination of retention.
[2] Samples heated at 600°C before determination of retention.

larger values generally being associated with the polyvalent ions. Values of "external" retention range from 2.0 percent for Mg^{2+} to 6.6 percent for Na^+. Despite the relatively high value for the Na^+-saturated clay, x-ray diffraction evidence showed that the 600°C heat treatment had apparently caused a completely irreversible collapse. A detailed interpretation of these results in terms of surface area and particle size for the various saturations is presented in a concurrent paper (Diamond and Kinter, 1958).

Glycerol Retention by Vermiculite

Glycerol retention was determined for two forms of a pure vermiculite furnished by John C. Hathaway of the U.S. Geological Survey: coarse flakes (about 200-mesh size) and a minus 2-micron size fraction prepared from the coarse flakes which were wet-ground for several minutes, ultrasonically dispersed at 600 kc for an hour, and further dispersed in a Waring Blendor.

A "total" retention value of 19.4 percent was obtained for the minus 2-micron fraction, similar to the "total" retention values of purified montmorillonites. A considerably lower "total" retention value, 7.8 percent, was found for the large flakes, indicating a difficulty of penetration of glycerol into the large flakes.

A retention value of 13.4 percent obtained for the fine fraction after K^+ saturation and drying indicates that about one-third of the layers are irreversibly collapsed by this treatment. It is apparent that the degree of collapse increases with increasing particle size, a 1.3 percent retention of the large flakes after K^+ saturation indicating almost complete collapse. Nevertheless, a small amount of reexpansion must still take place, since even this small value of retention could not result from adsorption on the relatively small external area available.

Glycerol Retention by Endellite

An investigation of the glycerol retention characteristics of endellite was carried out with a sample (R-137) from Chattooga County, Georgia, kindly furnished by H. L. Chamberlain, Division Three, Bureau of Public Roads. The source area was described by Broadhurst and Teague (1954). The basal spacing of the moist material was about 10A, which remained unchanged upon the addition of a glycerol-water solution. However, upon removal of most of the water by heating at 70°C (or extended air-drying), a spacing of 11.2A, indicative of a glycerol-endellite monolayer complex, was obtained. It is thus clear that this endellite does not exhibit preferential adsorption of glycerol in the presence of water.

Using aliquots of a suspension of the minus 2-micron fraction of the endellite, glycerol retention values were obtained for specimens (1) dried as in the normal procedure to constant weight at 110°C before addition of the glycerol solution, and (2) without predrying, by adding the glycerol solution directly to the clay suspension. The specimens were then heated in the presence of glycerol vapor to equilibrium at 110°C. In the first case, as expected, the endellite was irreversibly dehydrated by the pretreatment, and gave a glycerol retention value of only 1.5 percent, which presumably was due entirely to adsorption on external surfaces. However, the "wet"-glycerated samples retained 13.0 percent of glycerol, of which 11.5 percent is therefore attributable to adsorption on internal surfaces.

Glycerol Retention by Nonexpanding Clay Minerals

Glycerol retention data were obtained for specimens of several clay minerals and related materials which do not form regular complexes on interlayer surfaces. With these materials, retention is presumably due to adsorption on external surfaces only, except in the case of illite which may have a few randomly arranged, expandable layers. Table 4 indicates retention values for several illites, kaolinites, halloysites, the minus 2-micron fraction of angular crushed quartz (silica flour), and an Ando soil. As expected, the values are considerably lower than those of the expandable clay minerals. Values of about 5 percent for illites are probably due largely to the inherently small particle size, but possibly there is a minor effect of randomly arranged expandable layers. The kaolinites retained less than the illites, the variation in the several values probably being due to differences in inherent particle size, except for H-4 which is known to contain montmorillonite as a minor impurity. The values of 4.3 percent and 5.8 percent for the halloysites are somewhat high, when compared with the value previously obtained for the dehydrated Georgia endellite. Allophane has been reported as an impurity in the H-12 halloysite. The high retention by allophane is illustrated by the 14.6 percent value for the clay of the Ando soil.

FACTORS AFFECTING DETERMINATION OF RETENTION VALUES

A considerable body of experimental results were accumulated in connection with the development of the glycerol retention method. Certain of these data are discussed below to illustrate specific points having a bearing on the validity of the method.

Weighing Technique

Studies were made on the gain in weight (adsorption of moisture from the atmosphere) of glycerol retention specimens when removed from the oven for weighing. Using specimens of three montmorillonites, each specimen was brought to equilibrium with glycerol vapor, removed from the oven, cooled for 15 seconds on a cool enamel surface, placed on the pan of a preset chain-type analytical balance, and its weight noted at approximately 30 seconds after removal from the oven. The specimen was then left on the balance pan for 30 minutes, its weight being noted at intervals. Weight gain by an oven-dried

TABLE 4. — GLYCEROL RETENTION VALUES OF MATERIALS NOT FORMING "INTERNAL" COMPLEXES

Mineral		Size Fraction	Glycerol Retention Value, Percent
Illite:	H-35	Minus 2-micron	5.2
	H-36	Whole, passing no. 270 sieve	4.3
Kaolinite:	H-1	Minus 2-micron	1.3
	H-4	Minus 2-micron	3.3
	H-5	Whole, passing no. 270 sieve	0.8
	R-7	Minus 2-micron	1.4
Halloysite:	H-12	Whole, passing no. 270 sieve	4.3
	H-13	Whole, passing no. 270 sieve	5.8
Quartz:	R-65	Minus 2-micron	0.4
Allophane (Ando soil):	S-60	Minus 2-micron	14.6

specimen free of glycerol was also determined. A relative humidity of 85 percent in the laboratory provided an excellent opportunity for adsorption of water vapor.

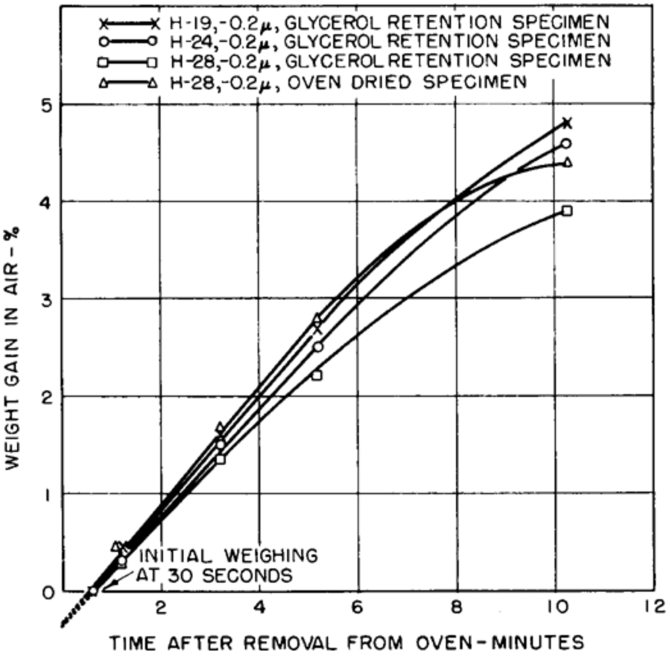

FIGURE 3. — Rate of water adsorption in air for three montmorillonite specimens at glycerol retention equilibrium and one specimen oven-dried at 110°C without glycerol. (Ambient temperature 72°F; relative humidity 85 percent.)

The data presented graphically in Figure 3 show that the rate of adsorption of moisture was linear for at least the first 5 minutes for all the samples. Projection of the weight-gain curves back to the time of removal from the oven indicates that the absolute error due to weight gain for a weighing at one minute after removal from the oven is at most about one-half of one percent of the weight of the clay, both for the glycerated specimens and for the plain clay. At lower humidities, the same samples would be expected to have smaller gains in weight during weighing, and, of course, clays other than montmorillonite would gain even less. It is clear that the rapid cooling and weighing specified in the procedure precludes weight-gain errors of any appreciable magnitude.

Sample Size

The effect of sample size on glycerol retention was determined with the minus 2-micron fraction of H-25 montmorillonite. The results indicate clearly that the equilibrium retention value is independent of sample size in the range covered, from 0.0150 to 0.2500 g of clay. Samples of any clay smaller than 0.0150 g are impractical because of weighing difficulties, whereas samples of montmorillonites larger than 0.2500 g require a considerable time to reach equilibrium. However, larger samples might be employed for determining glycerol retention on relatively inert materials such as kaolinite or fine quartz.

Thoroughness of Glyceration

To check thoroughness of glyceration, for the minus 0.2-micron fraction of H-25 montmorillonite, glycerol retention data were obtained by three procedures: (1) the normal procedure as outlined earlier; (2) ultrasonic dispersion (600 kc) of the powdered montmorillonite in water, drying the suspension in an aluminum cup at 110°C to form a thin oriented film, and adding the glycerol solution to this dried film; and (3) addition of the glycerol directly to an aliquot of an ultrasonically dispersed suspension of known concentration. The data showed no difference in retention between the first procedure and the second, the values being 18.1 percent in both cases. A slightly larger value, 19 percent, was obtained when the glycerol solution was added to the clay-water suspension. Whether this was due to a real difference or to volumetric inaccuracies is not known, but the small magnitude of the difference indicates that even for this very difficultly wettable montmorillonite, complete wetting and solvation are obtained in the normal procedure.

For all specimens examined, diffraction patterns obtained from upper and lower surfaces contained virtually identical basal peaks at about 14A, further indicating that solvation was complete and that at equilibrium the whole mass of each specimen was in the condition of a monolayer complex.

Effect of Temperature

To determine retention of glycerol by a typical montmorillonite at temperatures other than 110°C, samples of the minus 0.2-micron fraction of H-25 montmorillonite were dispersed ultrasonically and dried at 110°C to form films in preweighed aluminum cups. Individual specimens were brought to equilibrium at 70°, 90°, 130°, and 150°C, respectively. The results given in Figure 4 indicate an inverse linear relationship with temperature, with a difference of about 4 percent between the apparent retention at 70°C and that at 150°C. Other trials made with samples predried and equilibrated at the same temperatures provided data indicating that most of this apparent temperature effect was actually due to differences in the amounts of glycerol retained, rather than to differences in the amounts of water removed from the clay at various temperatures.

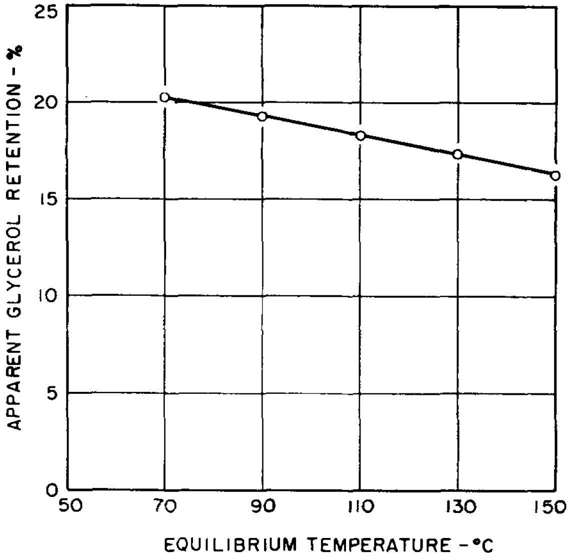

FIGURE 4. — Apparent glycerol retention of montmorillonite (H-25, –0.2μ) as a function of temperature of equilibrium. Retention based on weight of clay dried at 110°C.

"External" Glycerol Retention

Dyal and Hendricks (1950) proposed that a 600°C treatment of hydrogen-saturated montmorillonites collapsed the interlayer surfaces and permitted the retention of glycol only on external surfaces. They found experimentally that the glycol retention of H^+-saturated samples after this 600°C treatment indicated external surface areas of the same general order of magnitude as those measured directly by low-temperature gas adsorption. However, they found that a calcium-saturated montmorillonite gave high retention values after 600°C treatment, indicating that complete collapse of internal surfaces had not been attained. Bower and Gschwend (1952) published data comparing the glycol retention of a Wyoming bentonite saturated with various cations and then heated to 600°C, with glycol retention for the same materials not heated. The values after heating ranged from 9 percent of the unheated value, for the hydrogen-saturated sample, which presumably was completely collapsed, to values of well over 50 percent of the original, for sodium, potassium, and calcium saturation. Parts of the internal surfaces of the latter samples were obviously not irreversibly collapsed by the 600°C heating. It is thus apparent that the proposed 600°C heat treatment is effective only for some montmorillonites saturated with certain cations.

TABLE 5. — EFFECT OF HEATING TEMPERATURE ON THE IRREVERSIBILITY OF INTERLAYER COLLAPSE, AS INDICATED BY RETENTION VALUES AND X-RAY DIFFRACTION PATTERNS OF MONTMORILLONITES GLYCERATED AFTER HEAT TREATMENTS

Sample No.	Oriented-Aggregate Specimens on Ceramic Tile; Fraction Passing No. 270 Sieve, Natural Cation Saturation, 1-Hour Heat Treatment (°C)					Glycerol Retention Specimens, Minus 0.2-Micron Fraction, Cations Modified by Sodium-Bearing Dispersing Agent, 4-Hour Heat Treatment (°C)	
	350°	450°	550°	600°	650°	600°	650°
H-19	—	NC	C	—	—	C (1.8% retention)	—
H-23	—	NC	C	—	—	C (0.9% retention)	—
H-24	—	PC	C	—	—	C (1.9% retention)	—
H-25	—	NC	NC	PC	C	PC (11.0% retention)	PC (3.7% retention)
H-28	—	PC*	PC*	PC*	C	PC (11.4% retention)	PC (7.4% retention)
H-33a	NC	C	—	—	—	C (1.4% retention)	—

PC = partial collapse, at least some indication of 17.7A peak upon glyceration.
PC* = partial collapse, glyceration produces 13.2A peak indicating a random mixture of expanding and nonexpanding layers.
C = collapsed irreversibly, peak at 9.5-10A not affected by glyceration.
NC = not collapsed irreversibly, completely expanded to 17.7A by glycerol.

To determine the actual temperatures at which irreversible collapse occurs for certain of the API reference montmorillonites, an experiment was carried out as follows: Portions of the montmorillonites were lightly ground to pass a 270-mesh sieve, suspended in distilled water, and prepared as oriented aggregates on porous ceramic tiles. The specimens were oven-dried at 110°C, heated for one hour at various temperatures from 350° to 650°C, cooled, and glycerated, and x-ray diffraction patterns were recorded. The x-ray diffraction results are given in Table 5. The criterion of irreversible collapse was taken as complete absence of a 17.7A peak and presence of a peak at about 9.5A. The nontronite (H-33a) seemed to collapse irreversibly after 450°C heating; three of the montmorillonites (H-19, H-23, and H-24) after 550°C heating; and two other montmorillonites (H-25 and H-28) not until 650°C heating. It is to be remembered that these materials were still in their natural state of cation saturation.

In Table 5 are also listed glycerol retention values for the minus 0.2-micron fractions of the same montmorillonites preheated to 600°C for 4 hours. Because the samples were dispersed with sodium metaphosphate it is likely that sodium is the predominating cation. Glycerol retention values of 1 to 2 percent indicate complete collapse for all except H-25 and H-28, with values of 11.0 and 11.4 percent, respectively. Peaks at 17.7A in the x-ray patterns of these two samples treated with excess glycerol indicated a partial reexpansion. Heating H-25 and H-28 at 650°C for 4 hours resulted in somewhat lowered retention values (3.7 percent and 7.4 percent), but small 17.7A peaks obtained upon reglyceration indicate that the collapse was not entirely irreversible.

It is thus apparent that both the structure of a specific montmorillonite and the particular cation associated with it affect the irreversibility of collapse. It is also clear that realistic measurement of "external" glycerol retention of samples presumed to be irreversibly collapsed by a given heat treatment requires reglyceration of a portion of the heated material and examination by x-ray diffraction to determine whether partial expansion can still take place.

GLYCEROL RETENTION OF ARTIFICIAL MIXTURES OF MONTMORILLONITE AND KAOLINITE

The use of the glycerol retention value in estimating the amount of "expanding lattice" mineral in a given clay would require that retention be proportional to the percentage of such mineral in the clay. To check this point, retention values were determined for a series of mixtures containing various proportions of the minus 2-micron fractions of H-25 montmorillonite and H-1 kaolinite. As shown in Figure 5, the results verify that retention is proportional to the content of the montmorillonite. It should be noted that the minus 2-micron fraction of the montmorillonite is not a pure material, but contains appreciable quartz and other impurities. The kaolinite was selected because no trace of montmorillonite as an impurity was detected in it by x-ray diffraction.

Values of "external" retention (after 600°C heating) were determined but are not reported since it was discovered that heating at this temperature did not irreversibly collapse the montmorillonite against reexpansion with glycerol; the values are thus not true indications of external surface. However, a reasonable estimate for the retention on external surfaces of this montmorillonite is 1 to 2 percent, judging from data on other montmorillonites. Since the external retention for the pure kaolinite itself is 1.0 percent, for practical purposes the external retention is essentially constant for all mixtures of the two clays. Therefore, the values of both "internal" and "total" retention for a given mixture may be regarded as proportional to the content of montmorillonite in the mixture.

EFFECT OF PARTICLE-SIZE FRACTIONATION

Glycerol retention of nonexpanding clay minerals, being a phenomenon of adsorption on external surfaces only, should be expected to increase with

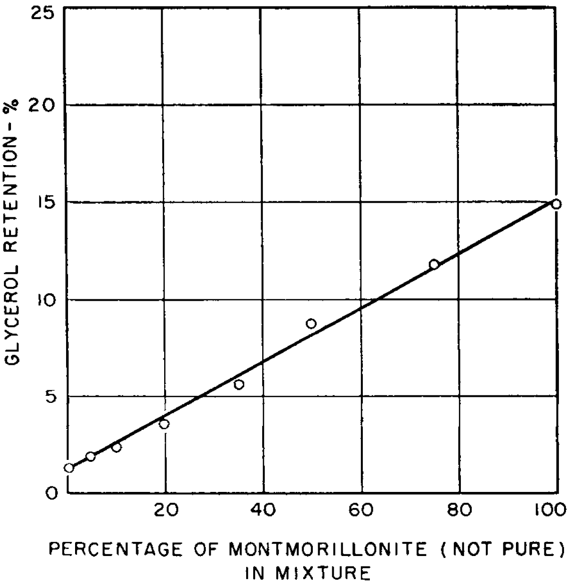

FIGURE 5. — Glycerol retention as a function of percentage of montmorillonite (not pure) in a series of artificial mixtures of montmorillonite (H-25, –2μ, aluminum saturated) and kaolinite (H-1, –2μ, aluminum saturated).

decreasing particle size. This point was verified by retention data obtained for three size-fractions of H-5 kaolinite (obtained by repeated centrifugal separation) as follows: 270 mesh to 2 microns, 0.4 percent retention; 2 to 0.2 micron, 0.8 percent retention; minus 0.2 micron, 1.0 percent retention. A retention value obtained for the whole material was identical to that for the 2 to 0.2-micron fraction, indicating that this fraction represents the bulk of this kaolinite. X-ray diffraction data, as well as the low retention value of the fine fraction, confirm that there is no contamination by montmorillonite in the sample.

MONOLAYER COMPLEXES OF ETHYLENE GLYCOL AND MONTMORILLONITES

Complexes of glycol and montmorillonites were not investigated in detail, but experimental work showed that a monolayer glycol complex analogous to that of glycerol does occur at 110°C in the presence of glycol vapor. In the results of the few trials performed, it was found that the weight of glycol retained was somewhat less than the corresponding weight of glycerol. The results were not conclusive, however, since some of the specimens were heated for only a few hours, and with others there was doubt as to the adequacy of the pressure of glycol vapor in the oven and of attainment of equilibrium. In view of the relatively high volatility of glycol, its monolayer complex is probably less stable than that of glycerol, and its quantitative maintenance at 110°C might therefore require a high, carefully controlled partial pressure of the vapor.

DECOMPOSITION TEMPERATURE OF GLYCEROL AND GLYCOL COMPLEXES

No extensive experimental work was undertaken to determine the maximum temperatures at which the monolayer glycerol and glycol complexes of montmorillonite might be stable, but some indication was sought in a few differential thermal analysis trials of several materials treated with glycerol and glycol. For clays such as kaolinite, or inert materials such as quartz and aluminum oxide, wetting with either polyalcohol gave rise to a sharp endothermic peak at the boiling point, about 200°C for glycol and 295°C for glycerol. Montmorillonites treated with glycol showed a boiling-point peak at about 200°C, and also another distinct endotherm at about 305°C. Montmorillonites treated with glycerol showed an endotherm at about 295°C in the general area of the boiling point, and in some cases there was evidence of two steps in the peak, one at 290° to 295°C and one at 305° to 320°C.

CONCLUSIONS

The following conclusions are drawn:

1. The two-layer glycerol complex of montmorillonites is not stable at 110°C, even in the presence of free glycerol vapor.
2. With a source of free glycerol vapor present, excess glycerol may be removed from montmorillonites, vermiculite, and endellite at 110°C, and an equilibrium attained at the condition of regular monolayer complexes.
3. Under the same conditions, a smaller but definite retention of glycerol occurs on the external surfaces of both expanding and nonexpanding clay minerals.
4. A simple gravimetric procedure is proposed which affords a quantitative measure of glycerol retention on both internal and external surfaces.

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