

Oct. 15, 1946.

F. J. EWING ET AL

2,409,263

DESICCANT

Filed April 13, 1943

6 Sheets-Sheet 1

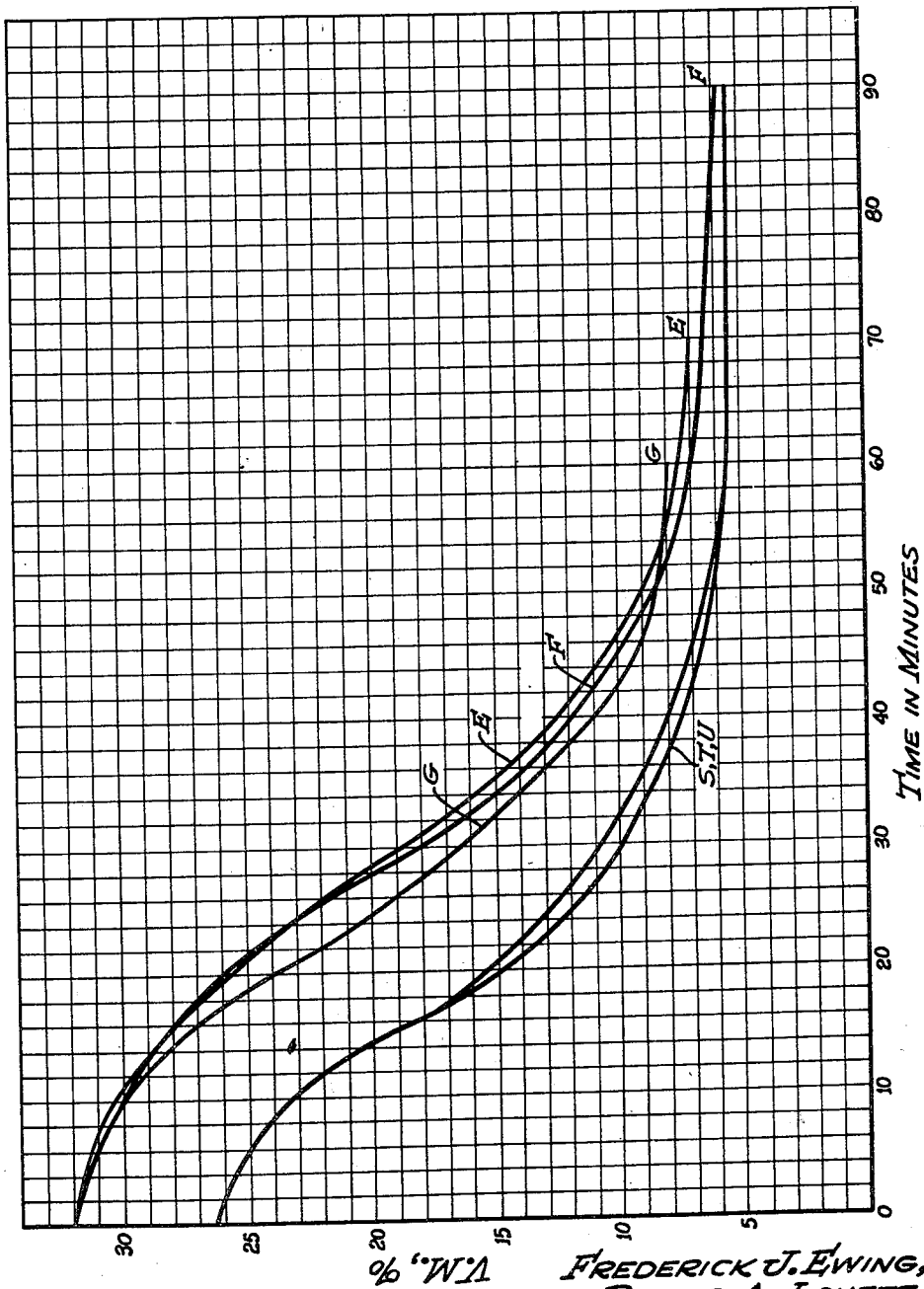


Fig. 1.

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6 Sheets-Sheet 2

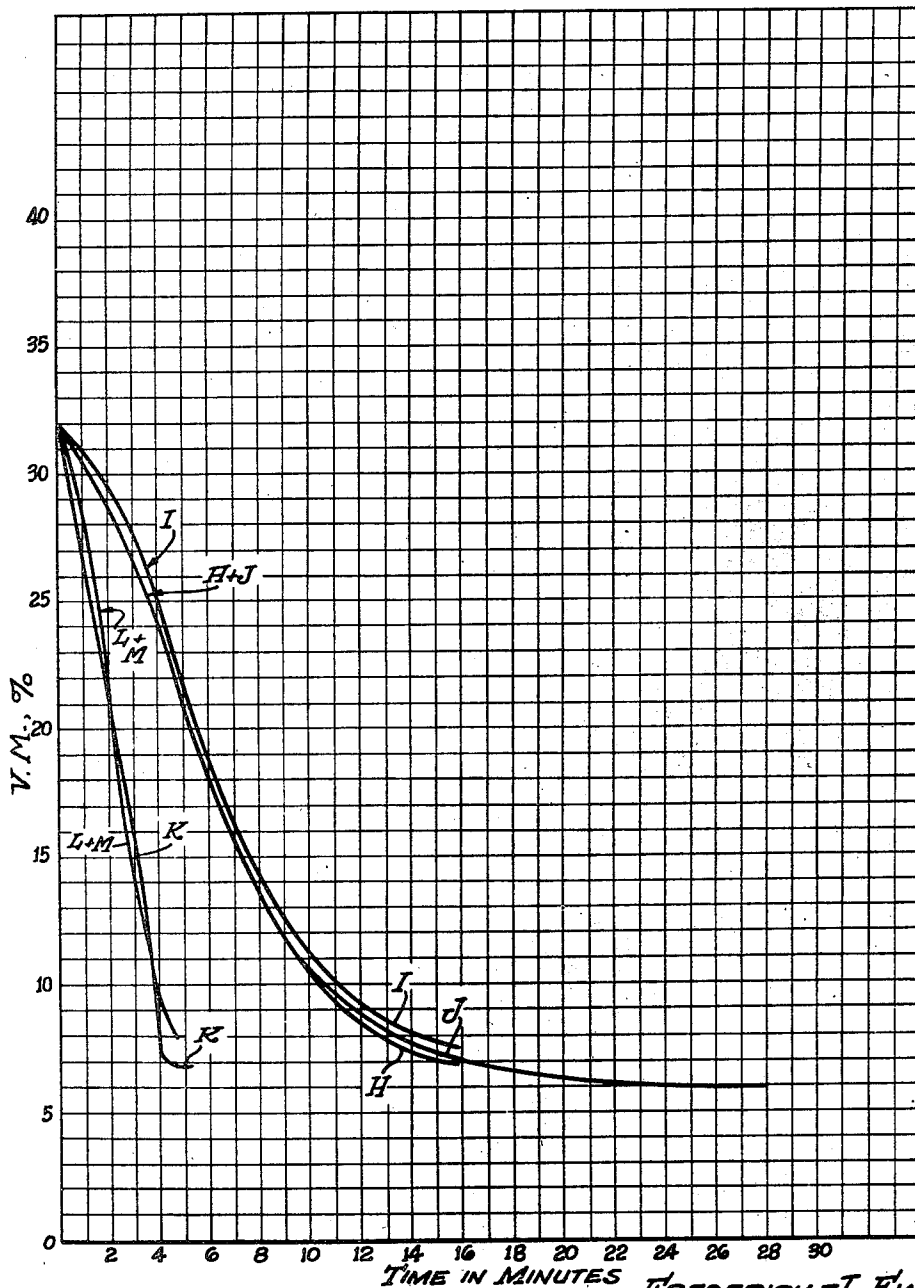


Fig. 2.

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DESICCANT

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6 Sheets-Sheet 3

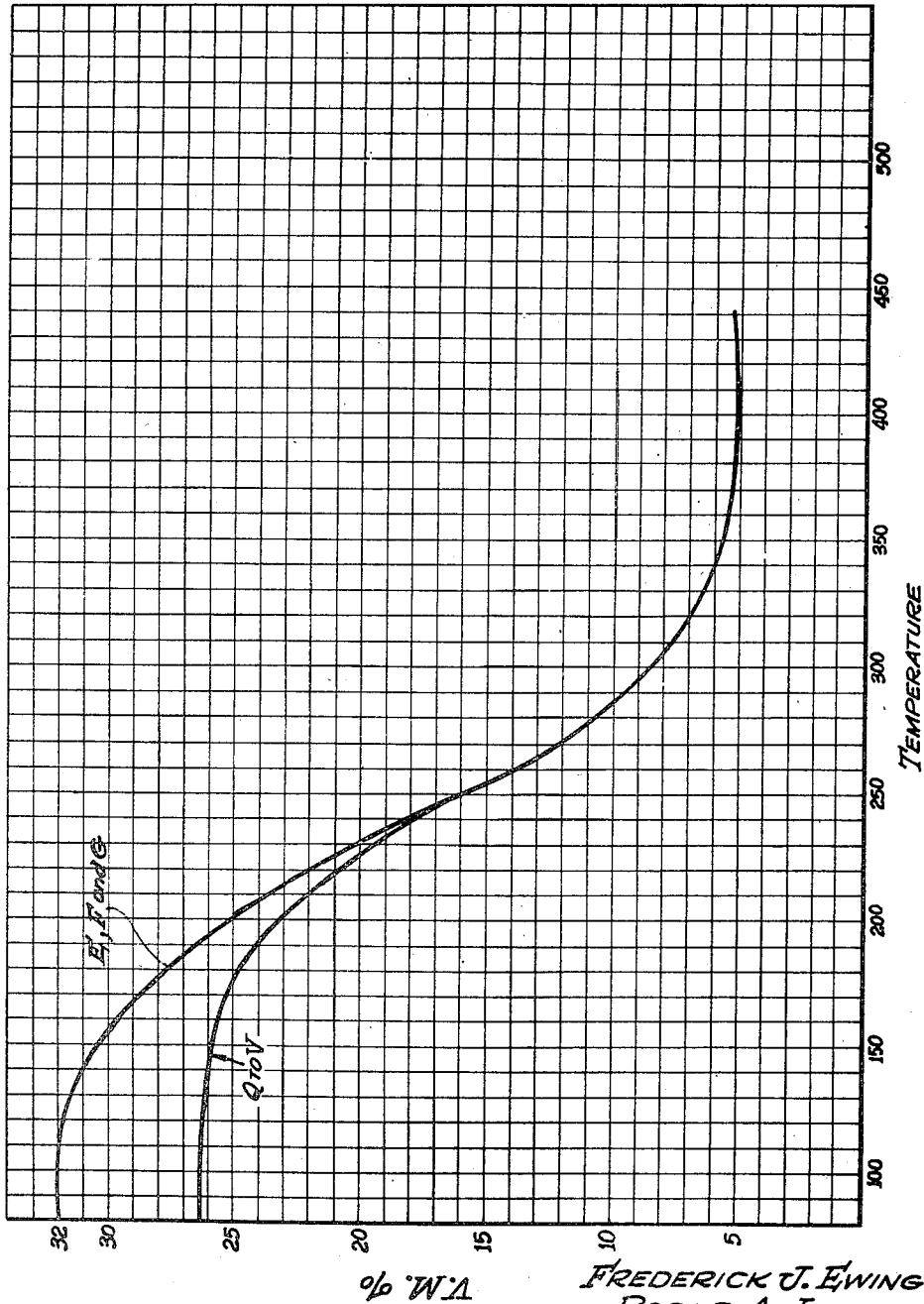


Fig. 3.

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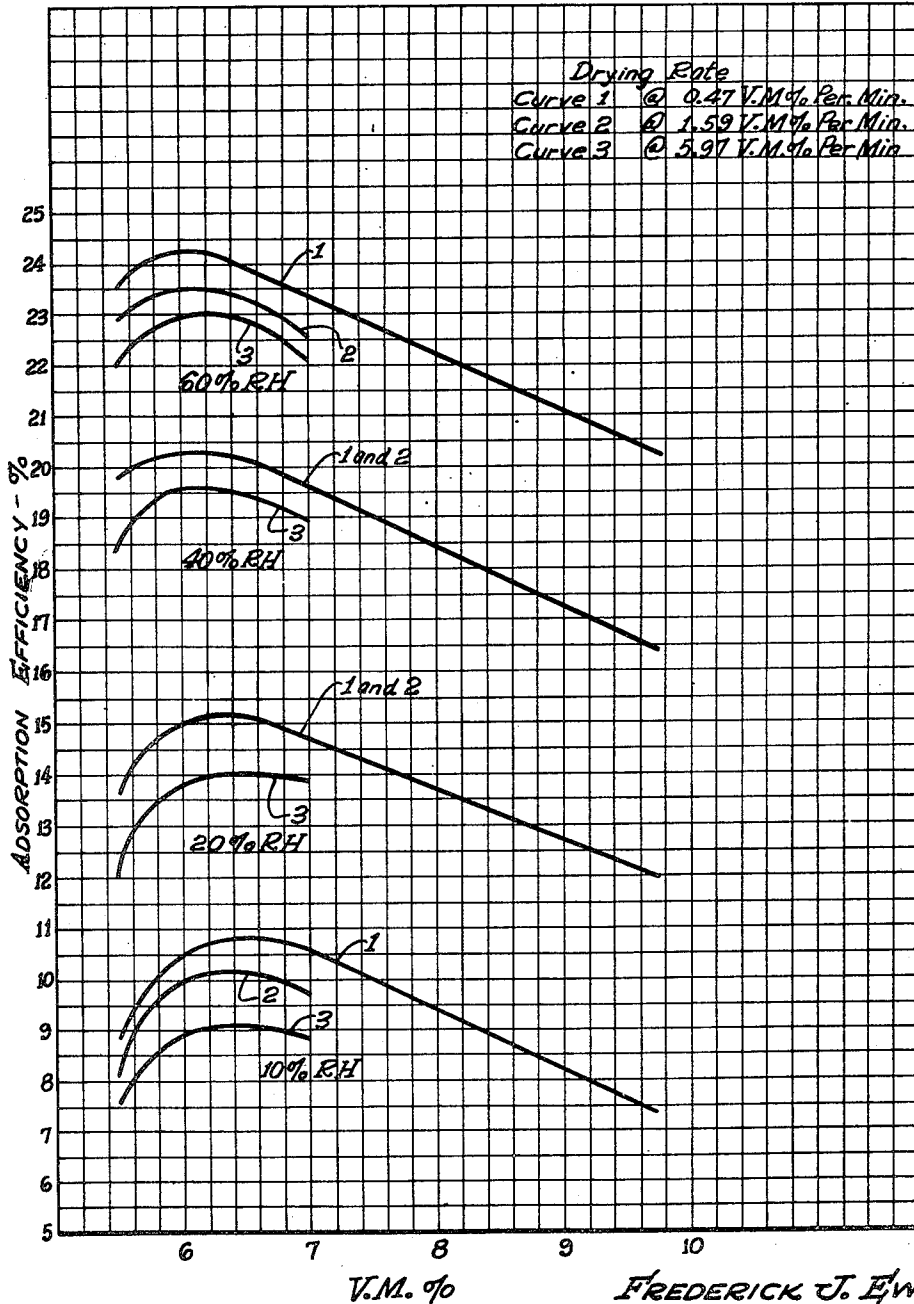
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Fig. 4.

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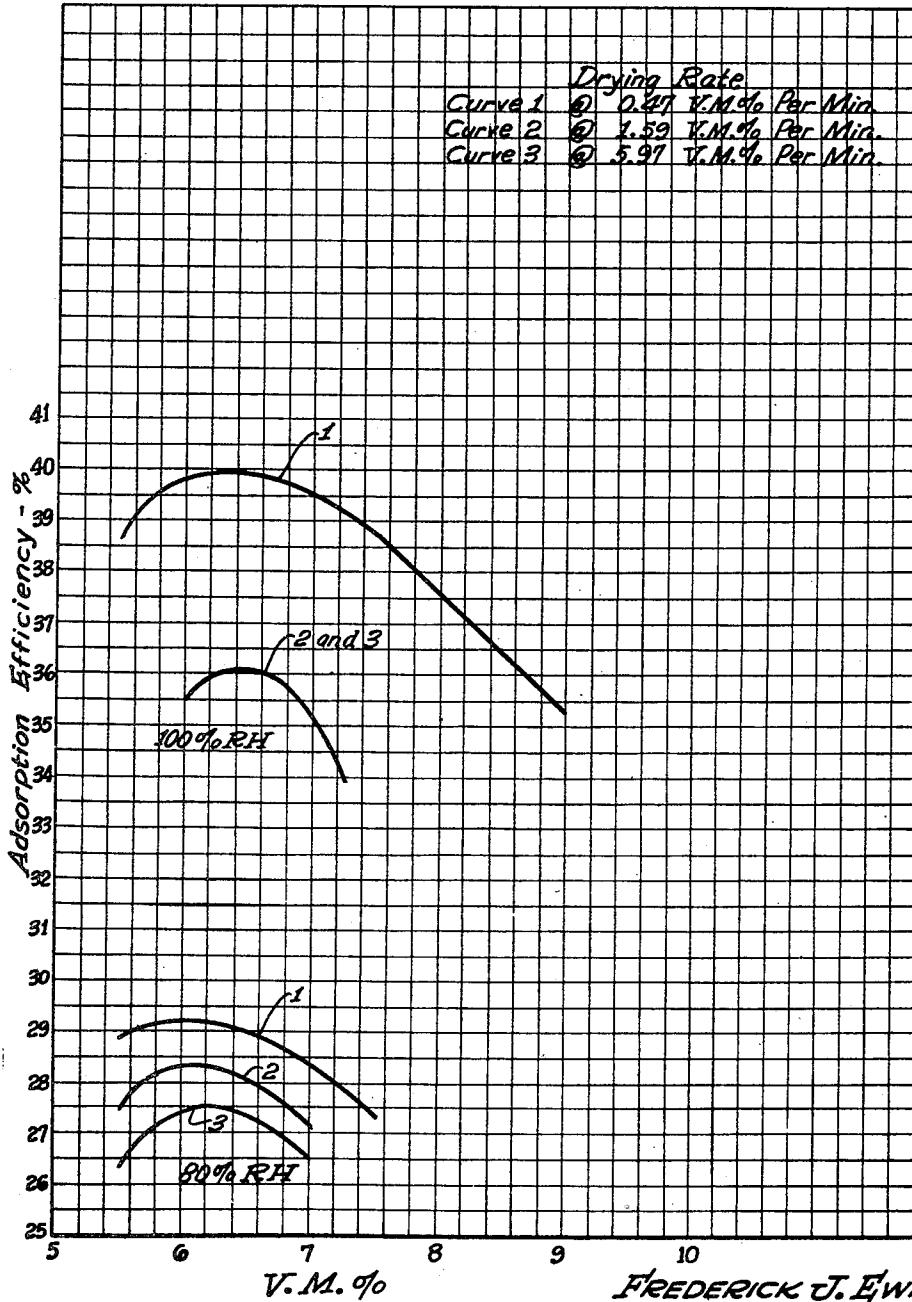


Fig. 4a.

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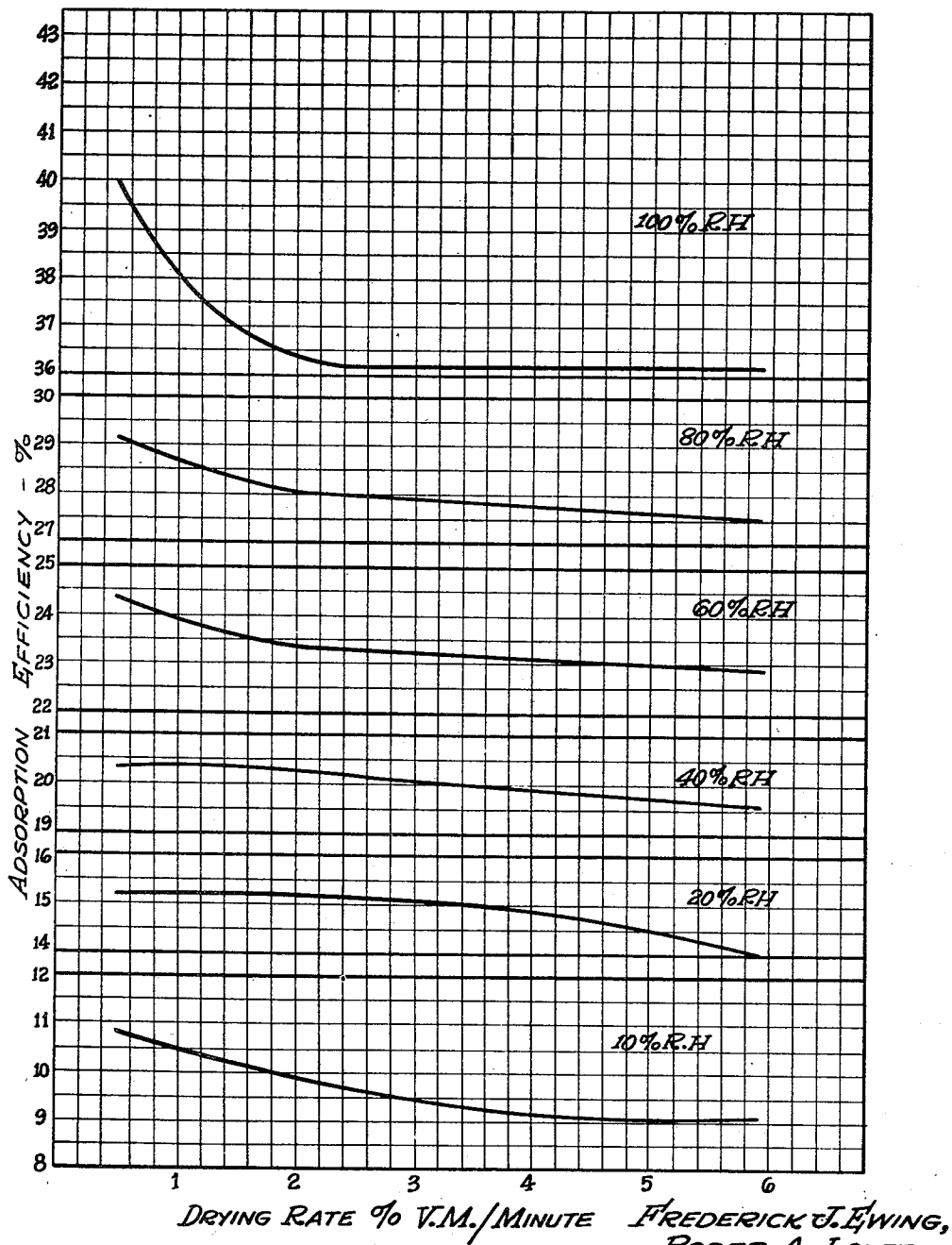


Fig. 5.

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UNITED STATES PATENT OFFICE

2,409,263

DESICCANT

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Application April 13, 1943, Serial No. 482,926

3 Claims. (Cl. 252-269)

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This invention relates to adsorbents for vapors, and particularly to desiccants; that is, adsorbents for water vapor, and to methods of producing such adsorbents from natural clays.

We have discovered that we may produce a highly efficient adsorbent for water vapor from montmorillonite clays. We are enabled to produce clays which are highly efficient as desiccants, particularly in adsorbing vapor from air of low humidity of about 30% or lower relative humidity, which are superior to known desiccants. We have accomplished this by drying the desiccants at a controlled rate and to a controlled final water content.

Desiccants are now employed for dehydration of air and/or other gases such as refrigerant gases. They are employed in dehydration of air and other gases in closed spaces in order to prevent corrosion, mold, or mildew. This is particularly important in shipment of metallic objects such as machine tools, ordnance or other metallic objects which are crated for shipment or storage. Packaged foods, such as fresh or dehydrated fruits, vegetables, and meat are also subject to spoilage in humid atmospheres. Lumber and wooden objects are subject to warping or so-called "dry rot." Packaged material must be protected from the attack of moisture if they are to be subjected, either in shipment or storage, to hot or humid climates.

In order to be effective for such purposes it is desirable that the desiccant have a high adsorptive efficiency for water, not only from air of high relative humidity, but also from air of low relative humidity. Essentially the objective to be obtained is to maintain the atmosphere enclosing the object to be protected at a low relative humidity.

It is therefore desirable to incorporate into the enclosed space, such as a car, ship, warehouse, or the package itself, a desiccant which has a high adsorptive efficiency capable of drying the air to a safe humidity. Experience has shown that such desiccant should have the ability to adsorb a large amount of moisture from air and must particularly have this high capacity when it is contacted with air having a relative humidity of 30 or less.

Useful adsorbents are such that can absorb at least 13% of their weight of water from an atmosphere of 30 relative humidity at a temperature of 75 to 85° F. The adsorptive efficiency at lower humidities may usefully be at least 10% by weight at 20 relative humidity and 5% by weight at 10 relative humidity. The higher the

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adsorptive efficiency, the more useful is the adsorbent.

Another important consideration is the hardness of the desiccant. It should resist abrasion and crushing. If it is not hard, but soft and friable, it will dust and contaminate the packaged material.

We have developed an adsorbent which has a much greater adsorptive efficiency at such relative humidities. Our material will, at temperatures of about 80°, absorb from 18 to about 20.5% of its weight of water at 40 relative humidity, from 17 to about 18.5% of its dry weight of water from air of 30 relative humidity, from about 13.5% to about 15% of its dry weight of water from air of about 20 relative humidity, and from about 8.5 to 11% of its dry weight from air of about 10 relative humidity. "Relative humidity" will be hereinafter indicated by the abbreviation "R. H."

Due to its greater adsorptive capacity we may use less of our desiccant to obtain the dehydration required to preserve the package at a relative humidity of 30 or less.

Our desiccant is also characterized by the fact that it is hard and not friable and substantially non-dusting under ordinary conditions of handling, packaging, and shipment. It will show about 1% loss by the standard method of determining hardness as given in "Army-Navy Aeronautical Specification," Specification No. AN-D-6.

In the following discussion we shall refer to "volatile matter" and "per cent volatile matter," or its abbreviation "V. M." By this quantity we mean the per cent loss as moisture of clay ignited at a temperature of 1700° F., in accordance with the method more fully stated hereinbelow.

We have found that we can obtain such a desiccant by controlled drying of montmorillonite clays of the sub-bentonite type, such as are activatable by acid treatment to produce useful oil decolorizing clays and cracking catalysts. Such clays are the substantially non-swelling bentonite clays as distinguished from the swelling type bentonites whose decolorizing power is not substantially improved by acid treatment. We have found that such clays, or such clays when activated by acid treatment, such as is used in making acid activated montmorillonite clay adsorbents and petroleum oil cracking catalysts, are converted to highly efficient desiccants if they are dehydrated to a volatile content of from about 5.5 to 8 V. M., and most efficient when brought, by proper drying procedures, to a V. M. content

of about 5.5 or 6 to 7%. This is somewhat greater than the theoretical hydroxyl water content of pure montmorillonite, which is about 5%. It thus appears that if the dehydration is carried out under such a condition as to remove substantially all free water, but not to remove the hydroxyl water content of the montmorillonite, we can obtain a highly efficient desiccant.

We have found that the rate of heating of the moist subbentonite clays, that is, the distillation rate of the moisture in the preparation of the desiccant, has a material effect on its resultant adsorptive efficiency. The removal of water at a moderate rate in bringing the clay to a V. M. content of 5.5 to 7% will give the most efficient adsorption.

There appears to be an optimum V. M. content for the dried clay produced which gives the greatest adsorptive efficiency.

In order to obtain the most efficient adsorbents, particularly for water vapor at low relative humidities, we desire to cause a relatively slow distillation, particularly during the drying of the clay from about 8 or 9% V. M. downward, and to reduce the water content of the clay to the region of the optimum value at which the maximum efficiency is obtained, and interrupt the heating to secure a clay of such optimum water content.

The process controls which produce our unique desiccant will be further understood from the following description taken together with the following drawings, Fig. 1 to Fig. 5, inclusive, which show the effect of the various heating variables on the desiccant efficiency and illustrate the desirable limits of heating which permit the attainment of the desiccants which constitute a preferred embodiment of our invention.

Fig. 1 to Fig. 5, inclusive, are charts showing plots of the data hereinafter presented.

The clay employed in the following examples was a montmorillonite clay of the substantially non-swelling sub-bentonite type produced at Cheto, Arizona, and having the following analysis based on a volatile free basis:

RAW CHETO—V. F. BASIS

Silica (SiO ₂)	67.3
Titanium oxide (TiO ₂)	0.3
Aluminum oxide (Al ₂ O ₃)	19.5
Ferric oxide (Fe ₂ O ₃)	1.8
Manganese oxide (MnO)	0.80
Magnesium oxide (MgO)	6.9
Calcium oxide (CaO)	3.2
	99.8

The original clay so processed has a natural V. M. of about 38 to 42% as mined, and may drop to 32 to 37% in transit to the mill.

In the following examples V. M. or per cent V. M. is determined as follows:

Approximately five grams of sample are placed in a porcelain crucible and quickly weighed to the nearest one-tenth milligram. After a preliminary heating at a low temperature, the crucible is ignited at a temperature of 1700° F. for approximately twenty minutes. After cooling in a desiccator, the crucible is again weighed. The loss in weight divided by the original weight of the clay multiplied by 100 is the per cent V. M.

The per cent gain in the weight of the clay when in equilibrium with air at various relative humidities, herein referred to as "adsorptive efficiency," was determined at a temperature of

80±1° F., according to the United States official methods specified by the Bureau of Ships and Interim Specifications issued November 1, 1940, No. 51S32 (INT), and Army-Navy Aeronautical Specification AN-D-6, issued November 20, 1942.

According to the method specified in this bulletin, ten gram samples of the clay are weighed into an adsorption bulb. The bulb is connected to the adsorption apparatus which consists of a train of bottles containing the sulphuric acid whose concentration is adjusted so that an air stream bubbled through these bottles will attain the desired humidity. The temperature of the sulphuric acid solution and the bulb is controlled to a substantially constant value, normally 80° F. Periodically, at intervals of one or two hours, the bulb is weighed, and the process is repeated until two successive weighings, approximately one hour apart, do not show a weight variation exceeding ten milligrams. The gain in weight divided by the original weight of the material multiplied by 100 gives the percentage by weight of water vapor that the material will hold in equilibrium with the air at the relative humidity attained in the saturators, and this quantity is hereinafter referred to as "adsorption efficiency."

The particle strength or hardness of the adsorbent is determined according to the method specified in the above bulletins. This method consists essentially of exposing the clay to the atmosphere of a room to permit it to come into equilibrium with the water content of the room. Then 150 grams of sample are introduced into an 8" #16 sieve backed by a #18 sieve and shaken in an apparatus which has a single eccentric, circular motion of about 290 R. P. M. and a tapping action of about 150 strokes per minute. The sieves are shaken for 15 to 20 minutes until not over 0.05 gram passes through the #18 sieve in one minute of continuous sifting. The fraction passing through the #16 sieve and onto the #18 sieve is used for the particle strength test. When testing larger size particles, a suitable quantity shall be ground to produce the required fraction through the #16 sieve onto the #18 sieve.

In order to determine this strength, 50 grams of the sample prepared as above-described are placed on an 8", #30 sieve which is backed by a #45 sieve and a retaining pan. Five copper discs of the size and weight of one cent pieces are placed on the #30 sieve, and the sieves are shaken for 15 minutes in the above apparatus. The sample remaining on the #30 sieve and the quantity which is contained in the retaining pan are weighed. We use the term "hardness" as the per cent retained on the #30 sieve. We use the term "friability" as the per cent falling through the #45 sieve and retained on the pan.

In the following examples, the clay was dried in an oven heated under controlled temperature conditions. The loss in weight of clay at various intervals of time was determined by weighing the clay without removing the clay from the oven. The clay was heated in accordance with the temperature schedules hereinafter set forth under each example.

Example A.—The clay at room temperature was introduced into the oven which was maintained at 350° F. during the entire drying process. The clay was held in the oven for four hours at this temperature. The clay was then removed to a desiccator and cooled. The volatile matter content of the cooled clay was 5.66%.

Example B.—The clay at room temperature was introduced into the oven maintained at 400°

F. during the drying process, and the clay was held in the oven for four hours. The clay was removed to a desiccator and cooled. The volatile content of the cooled clay was 5.56%.

Example C.—The clay at room temperature was introduced into the oven maintained at 500° F. during the drying process, and the clay was held for four hours in the oven. This constituted a shock heating suddenly to 500° F. The clay was removed to a desiccator and cooled. The V. M. of the cooled clay was 5.52%.

Example D.—The clay at room temperature was introduced into the oven maintained at 600° F. during the drying process, and the clay held for four hours in the oven. The clay was removed to a desiccator and cooled. The volatile matter was 5.07%.

The adsorption efficiencies of these clays are given in Table I:

TABLE I

Example	Percentage water vapor adsorption at indicated R. H.					
	10	20	40	60	80	100
A.....	8.8	13.7	19.8	23.4	27.5	35.1
B.....	8.0	13.1	19.2	23.2	27.5	35.3
C.....	5.6	11.9	17.9	22.5	26.6	34.4
D.....	3.15	7.8	15.3	20.7	25.0	34.0

In the above table, as in other like tables hereinafter given, the adsorption efficiency at any intermediate value of R. H. may be taken from curves drawn for the values of adsorption efficiency vs. R. H. These curves are not given herein in order not to multiply the number of figures. The values so given, however, may be taken as a disclosure of the adsorption efficiencies at intermediate values of R. H., such as 30 R. H., by the plotting of such curves, as will be understood by those skilled in the art.

Examples E, F, and G.—The clay at room temperature was introduced into the oven at 90° F. and the oven and clay were gradually raised in temperature. The clay was then removed at the various times indicated in the following table at the last V. M. recorded under each example, and cooled. During the cooling period some additional water was lost. The V. M. content of the cooled clay in Example E was 6.72%; in Example F it was 5.65%; and in Example G it was 7.61%.

The following Table No. II gives the temperature schedule; i. e., the heating rate of the clay in each of the examples is given. We give also the volatile content of the clay at each of the temperature levels and times.

TABLE II

Time, minutes	Temp., ° F.			Percent volatile matter		
	Example E	Example F	Example G	Example E	Example F	Example G
0.....	90	96	90	32.0	32	32
10.....	150	138	158	30.4	30	30
20.....	200	189	210	25.7	26	24
30.....	240	234	250	18.7	18	16.4
40.....	270	266	284	12.5	12	11
50.....	298	298	304	8.7	8.6	8.6
60.....	314	318	311	7.8	7	8.0
70.....	324	332		7	6.5	
80.....		356			6.1	
90.....		377			5.8	
100.....		400			5.8	

The adsorptive efficiencies of samples E, F, and G at the various relative humidities are given in Table III.

TABLE III

Percentage water vapor adsorption at indicated R. H.

Example	10	20	40	60	80	100
E.....	9.8	14.3	19.5	22.9	26.8	35.6
F.....	9.8	15.0	20.7	23.9	27.8	36.7
G.....	9.8	14.1	18.9	21.8	26.0	34.6

The drying curves of Examples E, F, and G are charted in Fig. 1 on which is plotted the V. M. content of the clay at various times, as given in Table II. In Fig. 3 we have charted the dehydration curve of the clay, giving the V. M. content of the clay at the various temperatures as reported in Table II.

Examples H, I, and J.—The clay at room temperature was introduced into the oven maintained at 350° F. during the drying process. The cold clay was introduced, rose to the temperature of the oven, and then was maintained at that temperature for a period of time. The clay was removed and cooled. The clay, as in the previous examples, lost some water while being cooled and the terminal V. M. was determined. The following Table IV gives the temperature schedule; i. e., the heating rate and the volatile matter content of the clay at each temperature level and time interval, thus giving the distillation rate. The terminal V. M. of the clay was: In Example H, 6.85%; in Example I, 7.15%; and in Example J, 5.89%.

TABLE IV

Time, minutes	Temp., ° F.			Percent volatile matter		
	Example H	Example I	Example J	Example H	Example I	Example J
0.....				32	32.0	32.0
3.....	300			26.3		
4.....		320	300		24.6	23.6
5.....	332		314	20.7		20.7
6.....		336	321		18.5	17.9
7.....	346			15.8		
8.....		344	330		14.1	13.7
9.....	354			12.0		
10.....		350	342		11.0	10.8
11.....	354			9.0		
12.....		351	346		9.2	8.9
13.....	356			7.75		
14.....		351	348		8.1	7.7
16.....	356		350	6.98	8.7	7.1
18.....			350			6.75
20.....			352			6.35
24.....			353			6.0
26.....			353			6.0
28.....			353			6.0

The adsorptive efficiencies of the clays of samples H, I, and J at the various values of R. H. are given in Table V.

TABLE V

Percentage water vapor adsorption at indicated R. H.

Example	10	20	40	60	80	100
H.....	9.5	14.3	19.7	22.6	27.0	36.2
I.....	9.5	14.0	19.4	22.3	26.7	33.7
J.....	9.9	14.9	20.3	23.6	28.2	35.3

The drying data of Table IV are charted in Fig. 2. In Fig. 2 is charted the time V. M. curve. From Fig. 2 it will be observed that the drying rate of samples H, I, and J in going from 32% V. M. to 7% V. M. has an average value of 1.59% V. M. loss per minute.

Examples K, L, and M.—The clay at room temperature was introduced into the oven at a

temperature of 550° F. The temperature of the clay rose rapidly. The clay was removed from the oven at the times indicated by the last V. M. reported in the table under each example, introduced into a desiccator and cooled. The V. M. content of the cooled clay was determined. The V. M. content in Example K was 5.85%; in Example L, 6.42%; and in Example M, 6.96%.

Table VI gives the value of the V. M. content of the clay and the temperature of the clay at various times during the drying operation.

TABLE VI

Time, minutes	Temp., °F.			Percent volatile matter		
	Example K	Example L	Example M	Example K	Example L	Example M
0.....				32	32	32
1.....	435	476	470	27.6	28.4	28.3
1.5.....						
2.....		482	490		20.3	21.7
2.5.....	450			17.9		
3.0.....		490	498		14.3	14.8
3.5.....	474			12.6		
4.0.....		500	510		9.1	9.1
4.5.....		506			7.74	
5.0.....						
5.25.....	524					
5.5.....				6.98		

The adsorptive efficiencies of the clays, samples K, L, and M at the various values of R. H. are given in Table VII.

TABLE VII

Percentage water vapor adsorption at indicated R. H.

Example	10	20	40	60	80	100
K.....	8.7	13.75	19.6	22.9	27.2	34.9
L.....	9.0	13.75	19.0	22.75	27.2	35.9
M.....	8.75	13.75	19.2	22.2	26.75	35.0

The drying data of Table VII are charted in Figs. 2 and 4. In Fig. 2 are charted the time V. M. curves. From Fig. 2 it will be observed the drying rates of samples K, L, and M in going from 32% V. M. to 7% V. M. had an average loss of 5.91% per minute.

Examples N, O, P, Q, R, S, T, U, V.—The raw clay used in this series was first air-dried to a V. M. of about 26% to permit ready handling. The air-dried clay at room temperature was introduced into the oven at a temperature of about 90° F. and the oven and clay were gradually raised in temperature. The clay was removed in the case of each example at various times, as indicated in the following table at the last V. M. recorded in the table for each example, and the V. M. content and adsorption efficiency determined. The drying data of Table VIII are charted in Figs. 1 and 3. In Fig. 1 are charted the time V. M. curves and in Fig. 3 the temperature V. M. curves. In Fig. 1 are charted the values for Examples S, T, U, V. The remaining examples fall closely on these curves. The drying rate of these examples was closely similar to that of Examples E, F, and G, giving effect to the lower initial V. M. content of the clays of Examples N to V. The average value of the drying rate for all the Examples E, F, and G, and N to V, inclusive, are substantially the same, and the average value of all the Examples E, F, G, and O to T, inclusive, was 0.47% V. M. per minute. Table VIII gives the V. M. content and the temperature of the clay at various times during the drying operation of Examples N to V, inclusive.

TABLE VIII

Time	Temp., ° F.			Percent volatile matter		
	Example N	Example O	Example P	Example N	Example O	Example P
0.....	90	92	90	26.35	26.35	26.35
2.5.....				26		
5.....	178	183	186	24.9	25.65	25.7
10.....	190	186	184	22.7	24.05	23.95
15.....	208	215	282	20.95	21.3	19.56
18.....	212			19.9		
20.....		236	295		17.95	17.75
24.....		248			15.0	
25.....			294			14.0
30.....			295			9.91

Time	Temp. ° F.			Per cent volatile matter		
	Example Q	Example R	Example S	Example Q	Example R	Example S
0.....	96	94	84	26.35	26.35	26.35
5.....	160	180	170	25.5	24.65	25.7
10.....	184	194	194	24.3	22.1	23.6
15.....	232	244	240	21.35	17.4	19.2
20.....	236	254	250	19	13.9	14.8
25.....	322	292	268	15	11.2	11.7
30.....	332	294	279	7.5	9.68	9.9
31.....	335			7.5		
35.....		324	288		7.87	8.55
40.....		342	300		6.48	7.77
45.....		360	320		5.88	
46.....		360			5.75	6.95
50.....			322			6.11
55.....			350			5.63
60.....			368			5.52
61.....			368			5.4

Time	Temp., ° F.			Per cent volatile matter		
	Example T	Example U	Example V	Example T	Example U	Example V
0.....	88	88	84	26.35	26.35	26.35
5.....	180	172	176	25.4	25.4	25.35
10.....	194	194	198	23.1	23.0	23.01
15.....	240	224	242	18.5	19.83	17.93
20.....	251	244	256	14.6	16.17	15.79
25.....	266	258	270	12	13.62	12.38
30.....	279	272	284	10.2	10.68	9.24
35.....	286	288	294	9.0	9.14	9.02
40.....	301	309	306	7.88	8.23	8.46
45.....	320	322	322	7.18	7.65	7.65
50.....	338	338	340	6.48	6.34	6.72
55.....	352	344	356	6.12	6.24	6.36
60.....	366	369	370	5.88	5.88	6.09
65.....	380	382	384	5.63	5.76	6.00
66.....			384			5.76
70.....	395	400		5.63	5.64	
75.....	410	412		5.63	5.57	
76.....	410			5.63		
80.....		428			5.57	
85.....		439			5.57	
90.....		438			5.57	
91.....		442			5.57	

The clay in the case of each example was removed from the oven at the times indicated for the last value of the V. M. recorded, placed in a desiccator and cooled.

The V. M. content of the cooled clay at the end of the drying process for each of the samples N to V, inclusive, is given in Table IX.

TABLE IX

Percent volatile matter

N	O	P	Q	R	S	T	U	V
18.73	12.9	9.75	7.47	6.1	5.89	5.62	5.57	5.76

The adsorptive efficiencies of the clays, Examples N to V, inclusive are given in Table X.

TABLE X

Percentage water vapor adsorption at indicated R. H.

Example	10	20	40	60	80	100
N.....	-2.5	1.5	5.3	8.75	12.6	24.3
O.....	3.3	9.1	12.7	16.2	20.3	33.2
P.....	7.5	12.0	16.5	20.25	25.0	35.3
Q.....	9.25	14.1	19.2	22.9	27.5	39.7
R.....	10.0	15.2	20.2	24.3	29.1	39.1
S.....	10.1	14.7	20.3	24.4	29.15	41.79
T.....	9.0	13.75	19.8	23.8	28.25	38.7
U.....	9.5	14.5	20.0	24.1	29.1	41.6
V.....	9.8	15.0	20.25	24.5	29.1	39.6

The drying of Examples E, F, and G, and N to V, inclusive, was conducted under approximately equilibrium conditions. In Fig. 3 we have charted the V. M. content of the clay at equilibrium at various temperatures. It will be observed that, giving effect to the varying initial V. M. content of the clay entering the drying process, the drying curves of all these clay samples are closely similar, showing a plateau at about a V. M. content of 5 to 7%, in which region the change in V. M. is substantially flat beginning at about 6% V. M. The knee of the curve as it enters the plateau curves is in the region of 6 to 7%. It is apparent that the loss of water in the region down to about 7% is of a different nature from that occurring in the region of 6% downward. This type of dehydration curve is well known to physical chemists and it would indicate that the montmorillonite crystal is losing its hydroxyl water of constitution when it is dried below about 6%. While we do not wish to be bound by any theory of the action of our drying process or of the adsorbent thus produced, it is important to note that this region of 6 to 7% corresponds with the region of optimum adsorption which we have discovered and as will be later described. It appears that the clay, if it is heated beyond a V. M. content of about 6 to 7%, results in a modification of the crystal structure of the montmorillonite resulting in some loss of hydroxyl water. It is of some interest to note that pure montmorillonite having the theoretical structure $(OH)_4Al_2Si_2O_{10}$ has a hydroxyl water content (i. e. water of constitution) of about 5%. The additional water which results in a V. M. content of 6 to 7% may well be the constitutional water of the impurities associated with the montmorillonite in the Cheto clay.

The sharp decrease in efficiency obtained by a small change in V. M. in going below about 6 to 7%, as hereinafter set forth, supports the view that the loss of hydroxyl water has a large deleterious effect on the surface activity and adsorptive properties of the clay.

Figs. 4 and 4a chart the effect of V. M. content produced at the various rates of drying upon the adsorption efficiency of the clay at various values of R. H. In these curves the V. M. is the terminal V. M. of the cooled clay of Examples A to V, inclusive, and the per cent adsorption at each R. H. is that here reported for such clay. At each R. H. there is a series of curves. As will be more fully described below, they represent the adsorption efficiency of the Examples E, F, G, and N to V, inclusive, dried at the slowest rate of about 0.47 V. M. per cent per minute. The Examples H, I, and J are dried at the intermediate rate of 1.59 V. M. per cent per minute, and Examples K, L, and M are dried

at the most rapid rate of 5.9 V. M. per cent per minute. It will be seen that for each rate of drying observed for the clays here reported, and at every value of relative humidity, there is an optimum V. M. content at which the adsorption efficiency is at a maximum and that this optimum resides in the range of 5.5 to 7% and more closely in the range of 5.5 to 6.5% V. M. The effect of departing from this optimum value of the V. M. content in either direction results in a decrease in the adsorption efficiency at each value of relative humidity, as is indicated in Table XI. In this table the adsorption efficiency at the optimum value is given as the range of adsorption efficiencies obtained for the range of drying rates there charted. The adsorption efficiency at the optimum V. M. is compared with the adsorption efficiency of Example D which had been dried to a V. M. content of 5.07% and Example P which had been dried to a V. M. content of 9.75%.

TABLE XI

Adsorption efficiency

R. H.	Example D	At optimum V. M.	Example P
10	3.15	9.2 to 10.8	7.5
20	7.8	14 to 15.2	12
40	15.3	19.6 to 20.3	16.5
60	20.7	22.9 to 24.3	20.2
80	25	23.5 to 29.2	25
100	34	36.2 to 40	36.3

It will be observed that the drying of the clay to a V. M. lower than about 5.5 to 6.5% has a substantial deleterious effect upon the adsorption efficiencies, particularly at the lower values of the relative humidity. As was said before, it is believed that this results from the fact that in going to a V. M. value below the optimum, we are entering the plateau region of Fig. 3 where losses of water of constitution occur and changes in crystal structure result in a destruction of surface activity.

While the specific values of the optimum here set forth may vary somewhat with clays from various beds, depending, it is believed, on the amount of impurities, it will be found that by applying the principles set forth above the limits of optimum V. M. content of sub-bentonite type of montmorillonite clays for the production of optimum adsorption efficiencies at each value of relative humidity may be readily determined. It is believed that the optimum will lie in the region of about 5 to 8%, depending upon the purity and quality of the clay, and this will occur at the knee of the curve of dehydration, such as is charted in Fig. 3. The exact V. M. percentage for optimum efficiency may also change with acid treatment of varying degree and intensity employed in acid activation of the clay. This value of the optimum efficiency may then be determined by plotting a chart like Fig. 3 or Fig. 4, by observing the change in water content at various temperatures and times during drying, and also by observing the per cent adsorption at a number of relative humidities sufficient in number to establish the curves in Fig. 4 for clays of varying terminal V. M. content.

As has been indicated above and as will appear from Fig. 4, the magnitude of the adsorption efficiency at all values of relative humidity depends on the rate at which the water has been removed as well as upon the V. M. content of the clay at the terminus of the drying period. As will

be observed from Fig. 4, at each value of the V. M. content and at each value of relative humidity, the adsorption humidity of the clay is higher the slower the rate at which the clay has been dried.

The effect of the drying rate upon the adsorption efficiency at each value of relative humidity is also shown in Fig. 5. In Fig. 5 is charted the adsorption efficiency of the clay at each value of the relative humidity taken at optimum V. M. content of the clay at such humidity, to wit, in the region of 5.5 to 6½% against the rate of loss of water. This rate of loss is taken as the quotient of the loss of water from the beginning of the drying process down to the time when the clay has a V. M. content of 7% divided by the time interval for such loss. This is termed the average rate of V. M. loss or the average drying rate. The terminal value of 7% was chosen as representing the break-point or knee of the drying curves shown in Figs. 1 and 2. At this point there is a large change in the rate of V. M. loss. Some other value close to 7% could be chosen as, for instance, 6 to 6½%, with a small change in the results attained. In the region of 8% V. M. and lower, major damage may result by overdrying. We desire to control the drying in that region to obtain a removal of water at a rate sufficiently low to give an optimum adsorption efficiency of high value. The average drying rate in this region is also included within the scope of the term "average rate."

It will be observed that the increase in the drying rate affects deleteriously the adsorption efficiency of the clay dried to its optimum V. M. content. As is evidenced by the curves of Fig. 5, this effect is most pronounced at the relative humidities of 10 and at 60 to 100. The clay is most sensitive to drying rate at such R. H. values. The clay is less sensitive in the region of 20 to 40 R. H. In fact, a more than threefold increase in going from a drying rate of 0.47% V. M. per minute to 1.59% V. M. per minute has but a small effect on the adsorption efficiency at 20 or 40 R. H. However, at 10 R. H. and at 60 and 100 R. H. major damage is done in going from 0.47% V. M. to about 1.59 per minute. The decrease in efficiency in going to the higher drying rate of 5.97% per minute is only moderate. This indicates that the degree of control of the heating rate which is necessary for the processing of this clay will depend upon what level of the humidity we desire to use for the clay. If we desire to operate at 30 R. H. or in the region of 20 to 40 R. H., we may dry the clay at a drying rate ranging up to about 4% V. M. per minute without materially affecting the adsorption efficiency of the clay when it is dried to the optimum range of V. M. However, if we desire that the clay be employed in adsorption in the region of 10 R. H. or in the region of 60 to 100 R. H., we will hold the drying rates to a closer control in the region under about 2% V. M. per minute, and we will get a greater enhancement if we hold the rate under about 1% V. M. per minute.

While the specific value of the drying rate to produce the effects herein set forth will change with clays from different beds, the general principles of the effect of the drying rate apply. Those skilled in the art will know how to repeat the tests here set forth to obtain the specific effects of the various drying rates in producing clays with varying V. M. within the range of about 5 to 8% and determine the adsorption efficiencies of the clay at each R. H. and V. M. content and thus obtain a series of curves such

as shown in Figs. 4 and 5 from which may be determined the specific values of the drying rate necessary to develop the desired adsorption efficiencies at the various relative humidities to which the clay is to be exposed, and by the application of these principles to determine the optimum conditions for the drying process to obtain the most desirable clay of highest adsorption efficiency under the conditions under which it is to be employed. It will be found that the slower the drying rate the higher the adsorption efficiency at all values of the V. M. content in the range of about 5 to 8% at all values of relative humidity, and that for each drying rate there is an optimum V. M. content within the range of about 5 to 8% and more particularly within the range of 5.5 to 7% where the optimum V. M. is to be obtained. By choosing the lowest practicable drying rate and by choosing the optimum V. M. content, the highest efficiency adsorbent and desiccant can be obtained by the application of the principles herein set forth.

In order to obtain the best results in the production of desiccants and adsorbents of highest adsorption efficiency, we prefer to employ drying apparatus which will expose the clay to the optimum temperature for production of the optimum V. M., and will attain the optimum V. M. at the optimum drying rate in such manner as to subject the clay uniformly to such temperatures and drying rates. We have found it desirable to avoid contact of the clay with gases of excessively high temperature or with hot metal surfaces under such conditions as might lead to partial overdrying of the clay or result in exposure of the clay to such high temperature as will produce excessive drying rates. In other words, while the average temperature conditions may nominally be within the range adequate, if the clay be uniformly heated, it is still possible, by reason of local hot spots and non-uniform distribution of temperature throughout the clay, for one portion of the clay to be overdried and another portion be underdried. In like manner it is possible, under such conditions, that part of the clay is subjected to an excessive drying rate while other parts of the clay are subjected to much lower drying rates. Such a clay when produced will be a mixture of good and poor adsorbent with an average value much lower than that which could be obtained had the clay been dried more uniformly at the optimum conditions.

We have found both rotary kilns and tunnel type driers satisfactory drying equipment, provided that they be of sufficient capacity to permit drying to take place gradually, as described above. It is desirable that such drying equipment be of sufficient size so that the drying load is satisfied by using gases at relative low temperature. We have found it useful to carry on our drying operation in a plurality of stages by employing a plurality of driers or tunnel type driers in which a plurality of zones of drying at different temperature and different humidity conditions can be maintained. The first stage of such plural-stage drying process may be operated at a low temperature level. For instance, in going down to about 8 or 10% V. M. to 20% V. M., the clay may be heated to a temperature of about 250 to 300° F. at a drying rate of about 4% V. M. per minute down to .5% V. M. or less per minute. In the second stage the clay is dried to about 5.5 to 7% V. M. at a drying rate of about 4% V. M. per minute or less at a temperature of 300 to 450° F.

In this second stage the drying rate may be controlled to a low rate so that the clay while drying down through the region where V. M. change may cause a substantial damage in adsorption efficiency, the drying rate may be closely controlled. By this separation of the drying process in the two stages, the load imposed on each drier is reduced, thus permitting more accurate control of the drying rate and temperatures. This permits of a more accurate control of the V. M. and drying rate in the second stage to produce the optimum V. M.

We have also discovered that by such procedure, not only will clay of high adsorption efficiency be attained, but the clay will also have a high hardness value such that it will not dust under ordinary mechanical handling, as when the clay is used as a desiccant in packaging various materials. Because of its high hardness value, the dry clay will not dust and pass through the meshes of the bags in which the desiccant is contained. As an example of the nature of the hardness values obtained when the desiccant is produced in accordance with the principles of our invention as herein set forth, the following may be taken as illustrative examples:

Example 1.—The clay was dried according to our process to a final V. M. content of 5.9%. When subjected to the hardness test previously described, .72% of the clay passed through a 30 mesh screen and .45% passed through a 45 mesh screen.

Example 2.—The clay was dried to a final V. M. content of 5.8% and its hardness values were 1% through a 30 mesh screen and .53% through a 45 mesh screen.

Example 3.—The clay was dried to a final V. M. content of 6% and then ground and graded into the following grades or types: type a; type b; type c; and type d. The screen analyses of the various types were as follows:

Type	Mesh size (screen number)	Type	Mesh size (screen number)
a	$+3=0\%$ $-3+6=65.9\%$ $-6+8=33.7\%$ $-8+=0.5\%$	b	$+6=0.0\%$ $-6+12=62.1\%$ $-12+18=37.8\%$ $-18+20=0.1\%$ $-20=9.2\%$
c	$+2=0.0\%$ $+45=99.2\%$ $-45=0.0\%$	d	$+2=0.0\%$ $+45=97.4\%$ $-45=2.5\%$

The index "minus" indicates through the screen, and the index "plus" indicates retained on the screen. The several types were subjected to the hardness test previously described with the following results:

	a	b	c	d
Particle strength percent falling through:				
Screen #30	0.76	1.2	0.93	0.87
Screen #45	0.40	0.47	0.53	0.64

It will be seen that by drying to approximately 6% V. M. we are able to produce a particle break-down of 1.2% and less through the 30 mesh screen and .64% and less through the 45 mesh screen. By a proper sizing of the material we can produce particles having as low as about .72% through the 30 mesh screen and .45% through the 45 mesh screen. Such material, experience has shown, will be non-dusting under ordinary mechanical handling and will not sift through bagging used for containing the material employed for packages in which it is used for controlling the humidity for the purpose of avoiding damage to the material packaged. A low friability is also of importance in installations requiring the use of the granular desiccant in large beds through which the fluid requiring drying is to be passed. Resistance of the granules to crushing and packing permits maintenance of minimum resistance to gas flow in such a bed, and also minimizes mechanical loss of desiccant.

It is entirely unexpected that large granules of the natural clay, of particle size such as shown in types a to d, above, would exhibit so great a degree of physical coherence when dried under conditions dictated by the desire of developing maximum adsorptivity or "porosity." As a matter of fact, however, the desiccant produced in accordance with the present invention is at once superior to synthetic commercial desiccants such as silica gel or activated alumina, both in terms of physical hardness and in adsorptivity at low relative humidities.

It is to be understood that the foregoing description of embodiments of our invention is for purposes of illustration, and modifications may be made therein without departing from the spirit of the appended claims.

We claim:

1. A desiccant consisting essentially of a native montmorillonite acid activatable sub-bentonite clay having a V. M. of about 5.5 to 7%.

2. The method of producing a desiccant from native montmorillonite acid activatable sub-bentonite clay which comprises reducing the V. M. of said clay to a V. M. of about 5.5 to 7% by heating to a temperature insufficient to modify the crystal structure of said clay, the reduction of V. M. being effected at an average rate no greater than about 1% V. M. per minute.

3. The method of producing a desiccant from native montmorillonite acid activatable sub-bentonite clay which comprises reducing the V. M. of said clay by heating to a V. M. of about 8% and further reducing the V. M. by heating to within the range of about 5.5 to 7% V. M. at a rate of less than about 0.5% V. M. per minute, all of said heating being at a temperature insufficient to modify the crystal structure of said clay, to produce a desiccant having an adsorption efficiency of at least about 17% at 30% relative humidity.

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