

Factors Affecting the Pyrophorosity of Spent Bleaching Clay

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Artificial cakes of bleaching clay/vegetable oil have been studied for their pyrophoric character using both Differential Scanning Calorimetry and a constant-temperature, fixed-interval, spontaneous heating (CaTFISH) test developed in this laboratory. It was determined that this is a two-step process involving a first-stage low-temperature spontaneous heating reaction followed by a second-stage high-temperature spontaneous heating reaction. The latter is characterized by charring and, in some cases, flaming combustion. A study of relevant variables has established that clay type, filter cake age, oil retention, moisture, and the presence of antioxidant significantly affect the spontaneous heating characteristics of clay/oil masses. Oil type was not found to be a significant variable in these studies.

KEY WORDS: Acid-activated montmorillonite, attapulgite, clay/oil mixture, oil-soaked clay, pyrophorosity, spent bleaching clay, spontaneous combustion.

Spent bleaching clays which have not received subsequent processing (i.e., steam blowing, water extraction, and hexane extraction) typically retain 20–40 wt% oil. Clay/oil masses such as these are susceptible to rapid oxidation to the point of causing spontaneous combustion (1,2,3). For those refiners unable to subject their spent bleaching clays to subsequent processing in order to recover entrained oil, the typical procedure is to remove the spent clay/oil mass from the filter press as quickly as possible (sometimes with a water spray) and get it into closed dumpsters for transport to landfill where it must be buried. Surprisingly, although there is wide-spread appreciation by the industry of the potential for spontaneous combustion by such clay/oil masses, virtually nothing exists in the literature regarding conditions and factors conducive to it.

This paper reports on our work to develop more rigorous methods to study spontaneous combustion of clay/oil masses, and identifies some of the more influential factors affecting it. Implications of the work in regard to practical methods to control the problem in an industrial setting are also discussed.

EXPERIMENTAL PROCEDURES

Materials. Predried, once-refined soya and linseed oils were obtained from vegetable oil refiners and used without further treatment. Bleaching clays were commercially available products and chosen to represent the two major categories of clay types in use today (i.e., acid-activated montmorillonite and raw attapulgite). Santoquin[®] antioxidant (6-ethoxy-2,3,4-trimethyl-1,2-dihydroquinoline; ethoxyquin) was obtained from Monsanto.

Differential scanning calorimetry. Experiments performed using differential scanning calorimetry (DSC) employed the Perkin Elmer High Temperature DTA Thermal Analyzer, Model 3600 (Perkin Elmer, Norwalk, CT). Low-temperature exotherms exhibited by clay/oil masses were generally obtained at scan rates of 10°C/min in an air atmosphere (30 cc/min flow) and utilized approximately 20 mg of the clay/oil mass. The temperature range employed was from ambient to 240°C. Calcined alumina was used as a reference material. When both low and high temperature exotherms were obtained, scan rates of 20°C/min in an air atmosphere (30 cc/min flow) were utilized. Precision by this method was generally quite good. The results of five runs of the low-temperature exotherm of an acid-activated montmorillonite/oil mixture are shown in Table 1.

TABLE 1

Precision of DSC Method

Measurement	Range	Mean	Standard deviation
Heat of reaction	61.5–66.1 cal/gm	63.0 cal/gm	±3.6 cal/gm
Onset temperature	70.1–76.4°C	72.5°C	±5.2°C
Peak temperature	159.4–162°C	160.5°C	±2.2°C

CaTFISH test. Experiments were also performed using a test method developed in our laboratory. Dubbed the Constant-Temperature Fixed-Interval Spontaneous Heating test (CaTFISH), it measures the minimum reaction temperature (MRT) at which charring occurs in (artificial) spent filter cake. To conduct the test, a cylindrical pellet of artificial spent filter cake² is placed in an oven at a fixed temperature for 1 hr and observed for a charring reaction; the oven temperature is increased in 5°C increments between each run until the MRT for charring is noted. Typically, the artificial filter cake was comprised of dried bleaching clay (110°C/4 hr) and refined soya or linseed oil. The standard pellet was produced from 5 gm of oil and 10 gm of bleaching clay using a piston and cylinder with an inside diameter of 3.1 cm (1.22 inches). When pressed at 5 lb/in² for 30 seconds, it produced a pellet approximately 2.6 cm high with a density of about 0.6 g/cc. Under these conditions, all of the oil mixed with the clay was adsorbed into the clay (i.e., the pellet weighed ~15 gm after pressing). To determine the MRT, batches of pellets (of different compositions) were run at a given temperature before raising the oven temperature 5°C and running the next batch of freshly pressed pellets. The lower the MRT, the more reactive and unstable the material. Additional pellets were run at temperatures above and below the MRT to confirm each MRT transition.

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²Large batches of artificial spent filter cake were prepared by mixing clay and oil and then placing the mixture in a sealed container and holding in a refrigerator at 4°C for 1–2 days before use.

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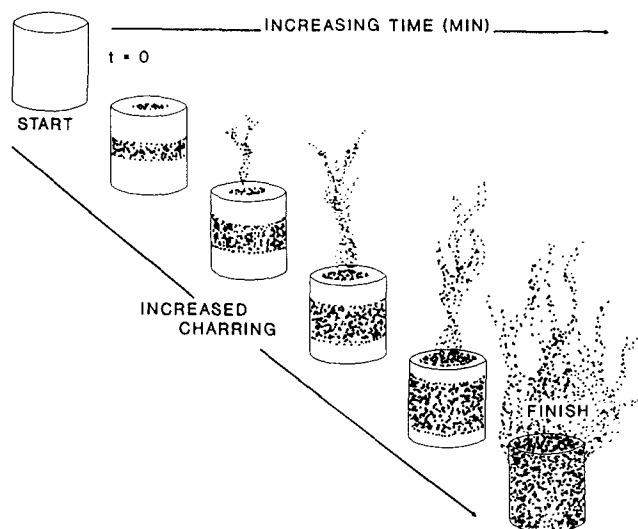


FIG. 1. Schematic of pellet charring once second stage spontaneous combustion begins at minimum reaction temperature.

The charring mentioned above initiates in the center of the pellet and travels outward. The charring "front" is characterized by the appearance of a black circle at the top of the pellet and a black ring girdling its sides (see Fig. 1). At this point, the pellet is smoking furiously. Once started, the front continues to expand and smoking persists even if the pellet is removed from the oven and placed in a hood away from heat. Very rapidly (within two minutes), the entire pellet is consumed by the front to give a black, smoking, and sometimes glowing briquette.

RESULTS AND DISCUSSION

Initial tests. Although a number of analytical methods do exist for determining the flash and fire points of liquids (and in some cases, solids suspended in liquids), most employ open flames (4) to initiate the combustion process or are applicable solely to liquids (5). These test conditions are so unlike those normally encountered during the spontaneous combustion of clay/oil masses in refineries that they cannot be used to obtain meaningful information regarding the combustibility of clay/oil masses. There are two ASTM methods for measuring spontaneous heating (6) which were considered, but the procedures described were impractical because they required a week or more to evaluate a given sample; since we contemplated doing at least some tens of samples, the investment in time was considered prohibitively excessive.

An ASTM test method for measuring the ignition temperature of granulated carbon (7) was also considered, and a variant of this method was used briefly during of our initial work. Our variant entailed placing a thermocouple inside a pellet of artificial filter cake in a chamber, then slowly raising the air temperature inside the chamber. The temperature was increased by means of a heat gun regulated by a temperature controller (the controller must have a "ramping" option). As the temperature is raised, the chart recorder documents the ambient and pellet temperatures; the spontaneous heating is detected by a rise in the pellet temperature above ambient.

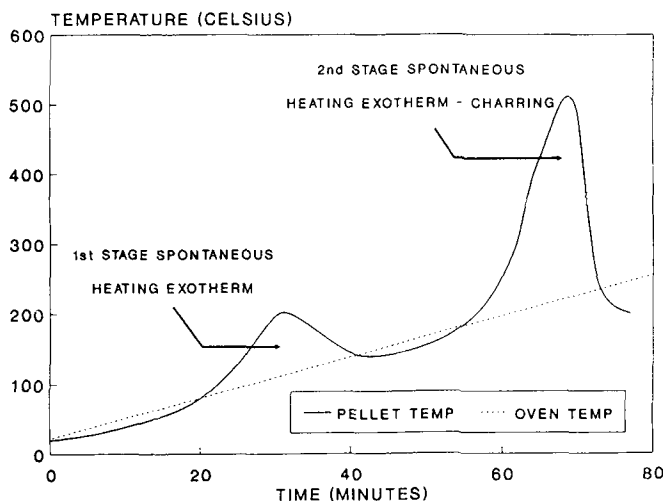


FIG. 2. Typical scanning thermometry run; first and second stage spontaneous heating. Oven temperature ramped.

A typical scan of pellet temperature (Fig. 2) shows clearly that the spontaneous heating (and ultimate combustion) of these clay/oil masses proceeds in two distinct steps: i) a low-temperature first-stage exothermic reaction; and ii) a high-temperature second-stage (even more) exothermic reaction characterized by smoking and charring. Unfortunately, this test method exhibited certain drawbacks: (i) the insulating property of the pellet kept the internal thermocouple below ambient temperature (except during an exotherm), hence it was difficult to determine the first point of spontaneous heating; and (ii) the location of the thermocouple was critical due to the high temperature gradient within the pellet. Because it was almost impossible to place the thermocouple in the same location each time, reproducibility between runs was quite poor (i.e., the shape and position of the curve did not stay constant from run to run). Thus, although the procedure was successful in showing the dynamics of the spontaneous heating process, the large variances obtained precluded using it quantitatively.

Differential scanning calorimetry. DSC, a standard thermal analysis technique, determines several parameters which might be expected to be associated with spontaneous combustion: i) onset temperature, the temperature at which the first sign of spontaneous heating is detected; ii) peak temperature, the temperature at which maximum exothermic reaction is achieved; and iii) the heat of reaction, estimate of total heat in calories per gram of clay/oil mixture. Using this method, a study was undertaken to screen a number of variables thought to affect spontaneous heating. Objectives of the study were twofold: to identify the most significant variables and to determine which DSC parameter(s) were most responsive to changes made in pellet compositions. These six variables were tested independently at two levels using a half-replicate fractional-factorial experimental design requiring 32 separate determinations. Table 2 lists the variable combinations and the DSC responses obtained. In these experiments, only DSC responses to the low-temperature first-stage reaction were measured based on

TABLE 2

Design Matrix Variables and Responses

Oil type ^a	Study variables					DSC responses		
	Oil retention ^b (wt%)	Moisture (wt%) ^c	Clay type ^d	Antioxidant (ppm) ^e	Cake age (hr)	Heat of rxn (cal/g)	Onset temperature (°C)	Peak temperature (°C)
S	40	0	AM	0	0.1	41.0	83.8	138.2
S	40	0	RA	0	24	90.4	109.2	138.2
S	40	0	RA	20	0.1	88.4	98.8	138.0
S	40	0	AM	20	24	44.9	85.1	147.6
S	40	10	RA	0	0.1	56.9	96.5	142.7
S	40	10	AM	0	24	37.1	84.0	136.8
S	40	10	AM	20	0.1	26.5	78.9	128.3
S	40	10	RA	20	24	43.7	98.8	137.9
S	50	0	RA	0	0.1	103.6	101.1	134.4
S	50	0	AM	0	24	72.1	87.0	149.3
S	50	0	AM	20	0.1	76.4	83.3	148.8
S	50	0	RA	20	24	107.9	111.0	137.2
S	50	10	AM	0	0.1	48.7	89.4	144.8
S	50	10	RA	0	24	68.1	101.7	140.8
S	50	10	RA	20	0.1	57.1	102.5	140.0
S	50	10	AM	20	24	35.5	79.6	132.5
L	40	0	RA	0	0.1	76.0	100.7	141.8
L	40	0	AM	0	24	56.9	87.8	132.0
L	40	0	AM	20	0.1	51.4	86.5	134.2
L	40	0	RA	20	24	81.8	101.7	136.7
L	40	10	AM	0	0.1	38.3	79.6	134.7
L	40	10	RA	0	24	52.6	102.8	142.8
L	40	10	RA	20	0.1	83.8	89.6	148.6
L	40	10	AM	20	24	23.6	80.0	135.7
L	50	0	AM	0	0.1	74.5	83.8	134.1
L	50	0	RA	0	24	104.4	108.3	138.1
L	50	0	RA	20	0.1	95.8	103.0	140.8
L	50	0	AM	20	24	83.9	91.3	133.7
L	50	10	RA	0	0.1	72.8	103.9	144.0
L	50	10	AM	0	24	50.9	87.8	138.6
L	50	10	AM	20	0.1	40.6	105.6	144.6
L	50	10	RA	20	24	77.3	106.9	143.5

^aOil type: S, soya; L, linseed.^bOil retention, (wt of oil/wt of dry clay) × 100.^cMoisture = 100 × [wt of as is clay - wt of dry clay]/wt of as is clay.^dClay type: AM, acid activated montmorillonite; RA, raw attapulgite.^eSantoquin®.

the reasoning that it is this step which acts at the trigger to the subsequent high-temperature charring reaction. That the low temperature exotherm is associated with an oxidative reaction was verified by running the same clay/oil mixture both in air and under nitrogen; only in the former case was the exotherm observed. It was assumed that low onset temperatures, low peak temperatures and high heats of reaction would all be responses indicative of more reactive systems (i.e., greater tendency for spontaneous combustion).

Table 3 presents selected data for the heats of reaction, onset temperatures, and peak temperatures, listed by main effect, or interaction effect. [An interaction effect quantifies the changes in the main effect of a variable (×1) as another variable (×2) changes, or *vice versa*. It is a response phenomenon that adds onto the contributions of the main effects. A positive interaction is a synergistic effect, and a negative interaction is an antagonistic effect.] The effect column shows the difference in the DSC

measurement between high and low values of each variable. For main effects, this difference is calculated simply by subtracting the average of the DSC measurements of the 16 high level samples from the 16 low level samples. For interaction effects, the algorithm is more complex but follows a similarly symmetrical calculation method. The data obtained were subjected to statistical analysis (DESIGN-EASE™; Stat-Ease, Inc., Minneapolis, MN) to determine which of the effects (variables) were large enough to be considered significant. Analysis of variance (ANOVA) calculations revealed several significant main and interaction effects which are noted in Table 3.

Figure 3 displays some of this data in graphical form and shows the effects of the main variables on the heats of reaction (first-stage spontaneous heating) as the variables go from the low to high level. The greatest positive effect is clearly clay type, followed by oil retention. Moisture shows a major negative effect. Thus a raw attapulgite type clay is more likely to undergo spontaneous

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TABLE 3

Effect of Variables on DSC Response Parameters

Variable	Difference of DSC averages	Significance ^a
Heats of reaction (cal/gm)		
Grand mean	64.47	0.0001
Oil type	4.14	0.0001
Oil retention	17.27	0.0001
Moisture	-27.24	0.0001
Moisture × oil retention	-6.21	0.0321
Clay type	28.64	0.0001
Antioxidant	-1.61	
Cake age	-0.04	
Onset temperature (°C)		
Grand mean	94.06	
Oil type	1.79	
Oil retention	5.15	0.0103
Moisture	-2.18	
Clay type	16.44	0.0001
Antioxidant	-0.30	
Cake age	2.25	
Peak temperature (°C)		
Grand mean	139.36	
Oil type	-0.73	
Oil retention	1.94	
Moisture	0.82	
Moisture × oil type	4.31	0.0006
Clay type	1.98	
Antioxidant	-0.20	
Cake age	-1.04	
Oil type × clay type	4.11	0.0010
Moisture × clay type	3.56	0.0035
Oil retention × clay type	-2.93	0.0138

^aProbability that the effect is due to error alone. Values <0.05 are considered significant and therefore real. Values >0.05 are not listed.

combustion than is an acid-activated bentonite type clay. Likewise, an increase in oil retention (from 40%-50%) is more likely to promote spontaneous combustion (however, as will be shown later, this conclusion must be modified when the study range is expanded). As might be expected, increased moisture decreases the likelihood of spontaneous combustion. As indicated in Table 3, a statistically significant interaction effect was found between oil retention and moisture levels. It suggests that the effect of moisture is greatest when oil levels are lower.

Based on the DSC studies, oil type, the presence of antioxidant and clay age were not found to be significant variables with regard to tendency for spontaneous combustion. Later experiments utilizing the CaTFISH test showed, however, that Santoquin® antioxidant does exert a beneficial effect if even higher (than 20 ppm) levels are utilized, and also that cake age has a very definite effect (this effect was apparently missed in the DSC studies because of the long time the samples were refrigerated before analysis).

With regard to oil type, although conventional wisdom holds (1,2) that more highly unsaturated oils will undergo spontaneous combustion most easily, that was not found

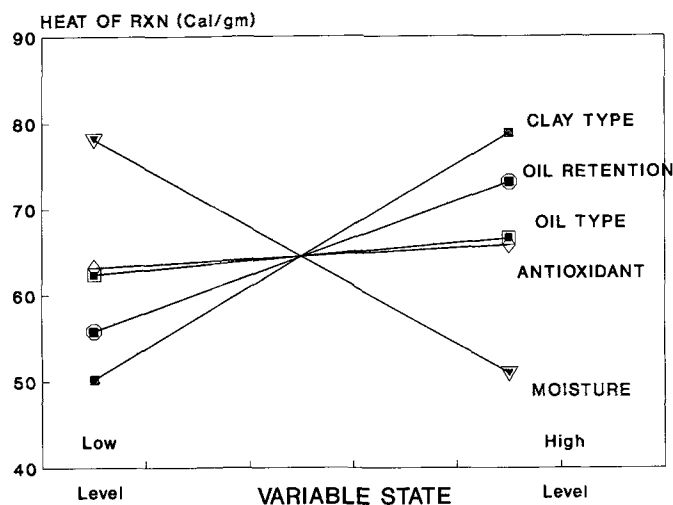


FIG. 3. Effect of main variables on heats of reaction at their high and low levels.

to be the case in these studies. Rather, we conclude that the level of unsaturation in the oil is relatively insignificant as a main effect (as regards pyrophorosity of clay/oil masses). According to Bailey (8), unsaturation has little, if any, effect upon the fire and flash points for pure oils. It appears from these data that clay/oil masses behave similarly. Some statistically significant interaction effects based on the peak temperature data were, however, detected and indicate that different oils may respond somewhat differently to moisture and clay type (Table 3).

In contrast to heat of reaction data, fewer relationships between the variables and DSC onset and peak temperature data were detected. Although clay type and oil retention were again identified as being significant variables on the basis of onset temperature response, none of the main variables was identified as being significant on the basis of peak temperature responses. In assessing the DSC method, heat of reaction data was found to be quite useful as a method to screen for significant variables influencing the spontaneous heating characteristics of clay/oil masses. Nevertheless, the conditions encountered during a DSC experiment (i.e., extremely small thermal mass of clay/oil mixture, relatively high surface to volume ratio, constantly increasing external temperature) are substantially different from those encountered in the real world (i.e., large thermal mass of spent filter cake, relatively low surface to volume ratio, static or falling external temperature). Because of concerns about the practical significance of results obtained by the DSC method, a method was developed which would more closely mimic the conditions found in the vegetable oil refining industry.

CaTFISH test: effect of time/temperature. The CaTFISH test uses the second-stage spontaneous heating and charring reaction as a visual indicator; it is the rapid, undissipated accumulation of heat from the first-stage reaction which triggers the second-stage reaction. Clay/oil pellets prepared under identical conditions were placed in an oven set at different (constant) temperatures, and then their internal temperatures were monitored over time (Fig. 4). Only in this particular experiment were in-

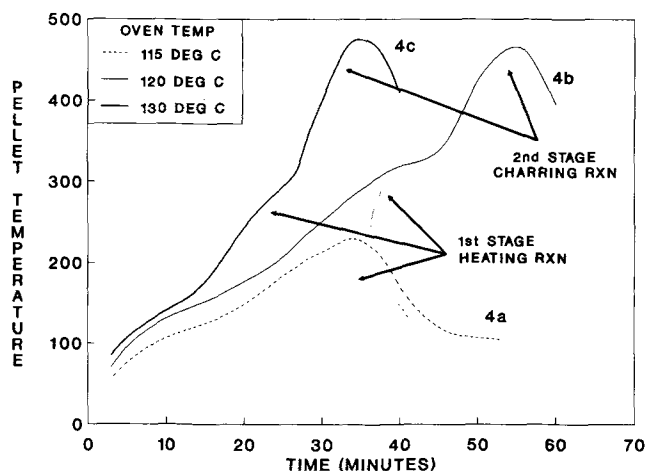


FIG. 4. Temperature increase inside clay/oil pellet as a function of (constant) oven temperature.

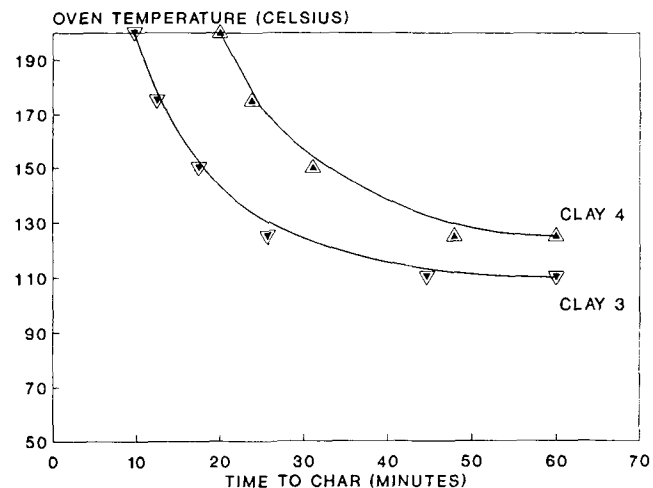


FIG. 5. Occurrence of spontaneous charring; time vs temperature relationship.

ternal pellet temperatures recorded by means of a thermocouple located in the center of the pellet to demonstrate the nature of the relationships between the oven temperature, the internal pellet temperature, and the charring process. Whether or not the charring reaction occurs depends on both the time and the temperature. As shown (curve 4a), if the oven temperature is too low, the pellet will undergo the first-stage spontaneous heating reaction, but will fail to trigger the second-stage charring reaction because the heat generated in the first-stage reaction is dissipated before the second-stage initiation temperature has been reached. At a somewhat higher oven temperature (curve 4b), undissipated heat from the first-stage reaction is sufficient to further heat the pellet and trigger the charring reaction. At an even higher oven temperatures (curve 4c), the same result is obtained, but the entire process is accelerated.

In the standard CaTFISH test, as described in more detail below, temperatures of the pellets were taken to be equal to the oven temperature. MRT's were then defined as those oven temperatures external to the pellet which would cause charring. Since time to trigger the second-stage reaction is temperature dependent, work was also done to standardize the time component of the CaTFISH test. A series of experiments were conducted where clay/oil masses utilizing two different grades of acid-activated montmorillonite were subjected to lower and lower oven temperatures. As shown in Figure 5, both clays take increasingly longer periods to achieve charring as the oven temperature is decreased. It was found, however, that if charring had not occurred after 1 hr of heating (at a given temperature), then no amount of additional heating at this temperature would cause it to occur. On this basis, the standard heating time in the oven was set at 1 hr. In some cases, longer standard heating times may be required (e.g., when using oils with better thermal stability, or when using other kinds of sorbent

materials). The minimum oven temperature which will cause a pellet (heated for 1 hr) to undergo the charring reaction is defined as the minimum reaction temperature (MRT). In Figure 5, clay 3 has an MRT of 110°C; clay 4, an MRT of 125°C. Since clay 3 exhibits the lower MRT, it would be considered the more reactive (potentially more pyrophoric) clay when mixed with oil.

Effect of oil retention and moisture. Using the CaTFISH test, the same set of variables as used previously was re-examined to determine their effect on the MRT's of clay/oil masses. Aside from clay type, two other variables (moisture and oil retention) had been previously identified as being significant with regard to their ability to affect pyrophorosity. A set of clay/soya oil pellets was prepared in which moisture content was varied from 0-30% and oil retention was varied from 30-90%. The MRT data obtained from the CaTFISH test were then used to construct a response surface as shown in Figure 6. The response surface plot gives a clear visual representation of the MRT response over the region measured. These data were obtained using clay 3 (an acid-activated montmorillonite type clay). While the response surface for other clay samples should look similar in general, shifts in the coordinate positions of the MRT responses as a function of oil retention and moisture levels would be expected to be different in detail for different clays.

The most obvious feature of the response surface is a minimum in the region of 50-60% oil retention. Since lower MRT equates with greater reactivity, this minimum represents the least stable condition of the filter cake. In accord with the DSC data previously discussed, it can be seen that increasing the oil retention of the cake from 40% to 50% decreases the MRT (i.e., increases the likelihood of spontaneous combustion). However, once conditions for maximum cake reactivity are achieved (in the region of 50-60% oil retention) a further increase in oil content actually decreases the likelihood of spon-

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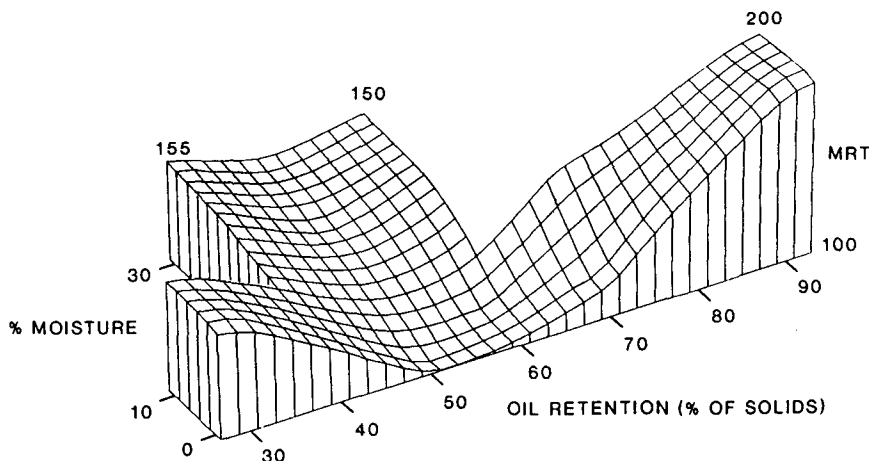


FIG. 6. Response surface—minimum reaction temperature ($^{\circ}\text{C}$) vs moisture and oil retention.

taneous combustion. A likely explanation is that at higher oil loadings, pores in the filter cake become increasingly filled. Hence, the clay/oil system begins to behave more like bulk oil; attack by oxygen, the primary initiator of the spontaneous combustion process, is restricted because available pore surface area is decreasing. At lower oil loadings (below 50% oil retention), available pore surface area is high, but now the amount of oil to sustain spontaneous combustion is decreasing. Only in the region of 50–60% oil retention is the balance between available pore surface area and oil content such that optimal conditions for spontaneous combustion are obtained.

As is also apparent from examination of Figure 6, increasing moisture significantly decreases the chances of spontaneous combustion. Although moisture levels of filter cakes from typical refinery operations would be quite low coming from the filter press, these data clearly indicate the beneficial effect of adding moisture as a means of controlling spontaneous combustion of clay/oil masses. However, the moisture would have to be intimately mixed with the clay/oil mass by mechanical or chemical (surfactant, etc.) means.

Effect of filter cake age. Figure 7 depicts the effect of cake age vs MRT for pellets prepared from artificial filter cake stored under two different sets of conditions. The inference to be made from these data is that freshly prepared filter cake is considerably less reactive than is filter cake which has had a chance to undergo some degree of oxidative attack. After one day of storage in a sealed container at room temperature, the filter cake has reached maximum reactivity (i.e., exhibits a minimum MRT). Subsequent to that, the tendency to undergo spontaneous combustion begins to lessen. In contrast, storage at 4°C in a refrigerator significantly lengthens the time required to reach maximum reactivity. A plausible explanation for these results is that certain species of oxidation reaction products are produced that are more labile (more likely to undergo exothermic decomposition leading to a rapid build-up of undissipated heat). However, because these species are inherently metastable, their population

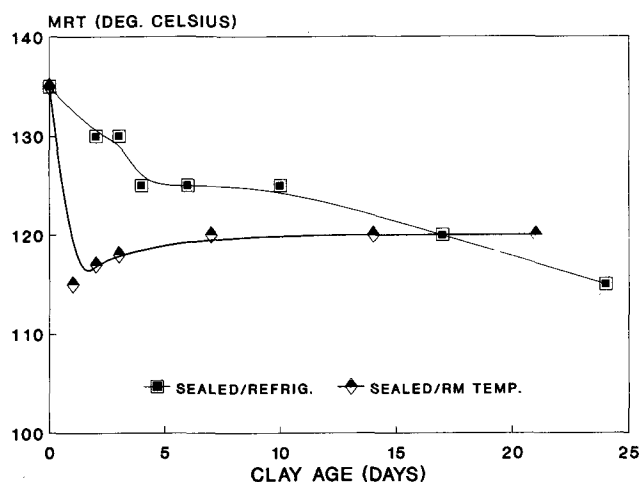


FIG. 7. Effect of clay aging conditions on minimum reaction temperature.

quickly reaches a maximum (at room temperature) and then begins to drop off as more stable (terminal) oxidation products are formed. While the reaction sequences followed in high-temperature triglyceride autoxidations are quite complex (9,10), and possibly even more complex in the case of clay/oil masses where catalytically active surfaces are present (11,12), it can be speculated that the build-up of hydroperoxides or hydroperoxy epoxidized (13) may be associated with the most reactive stage of aged filter cakes. These compounds are known to be quite unstable, and might be expected to pass through a population maximum that would mimic the aging characteristics just described.

Regardless of the correct interpretation for these results, the practical consequence is that considerable care must be taken to insure that the cakes are of the same age when using the CaTFISH test to evaluate the pyrophoric properties of clay/oil masses. As shown in Figure 7, clay/oil masses which are refrigerated in sealed

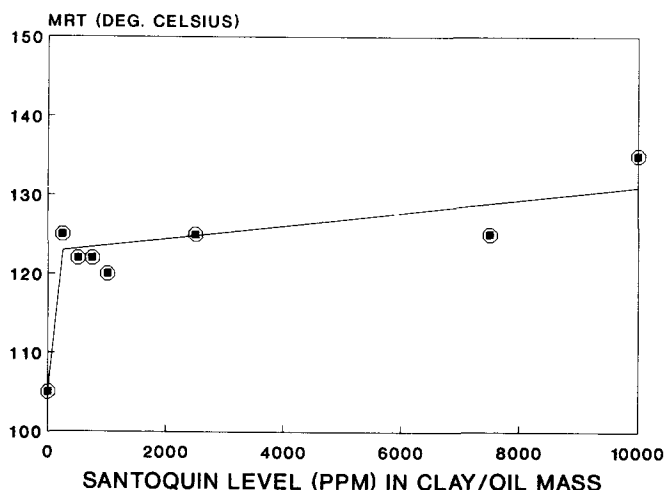


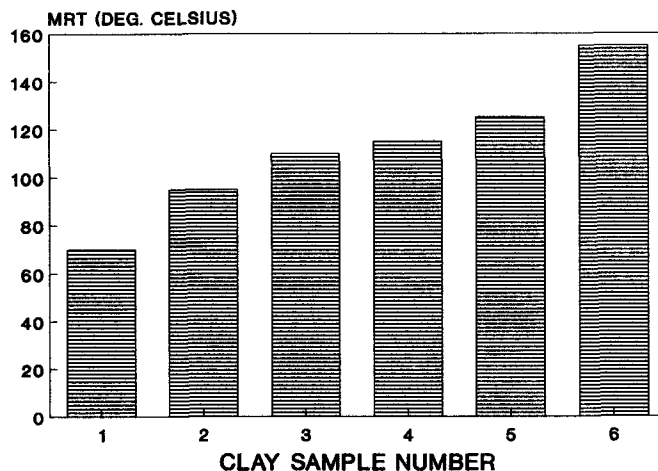
FIG. 8. Effect of Santoquin level on minimum reaction temperature (CaTFISH test).

containers exhibit a plateau in spontaneous heating reactivity after being held for 4–10 days. Although most of our work involved refrigerated samples held for 1–2 days, we now believe samples held for 4–5 days would give even better precision. From a refinery point of view, these data suggest that care should be taken to remove spent filter cake from the refinery location as quickly as practical since it appears that the likelihood of undergoing spontaneous combustion actually increases with time over the first 24–48 hr.

Effect of antioxidant. Figure 8 shows the results of incorporating ethoxyquin [a well-known antioxidant used to control the spontaneous combustion of fish meal (14)] into clay/oil masses which were studied by the CaTFISH test. In these experiments, the antioxidant (Santoquin®) was dissolved in the oil before it was mixed with the clay and pressed into a pellet. Although there is some scatter in the data, there is clearly a beneficial effect with regard to decreasing the spontaneous combustion of the clay/oil mass with inclusion of the antioxidant at a level of 100 ppm or greater. In fish meal, ethoxyquin is typically used at a level of 400 ppm (12). Of course, other antioxidants can be used to reduce the rate of oxidative attack on oil (15); however, these were not included in the present study. Whether they would work similarly to ethoxyquin with regard to controlling the spontaneous heating characteristics of clay/oil masses is, for now, an open question. At the refining level, what these data suggest is that an antioxidant such as ethoxyquin should decrease the tendency toward spontaneous combustion. Practically, whether it could be mixed with the final amount of oil charged to the filter press, or somehow sprayed on the spent cake after discharge from the press is a subject for additional study. Santoquin® is available in water soluble form, and could be mixed with clay using a water/surfactant spray, for instance.

Effect of clay type/intrinsic oil retention. As already indicated on the basis of DSC studies, clay type and oil retention exert strong effects on the pyrophorosity of clay/oil masses. However, precisely because both parameters are influential, some care must be exercised in using either DSC or CaTFISH data to draw conclusions

MRT AT 50% OIL RETENTION



MRT AT INTRINSIC OIL RETENTION

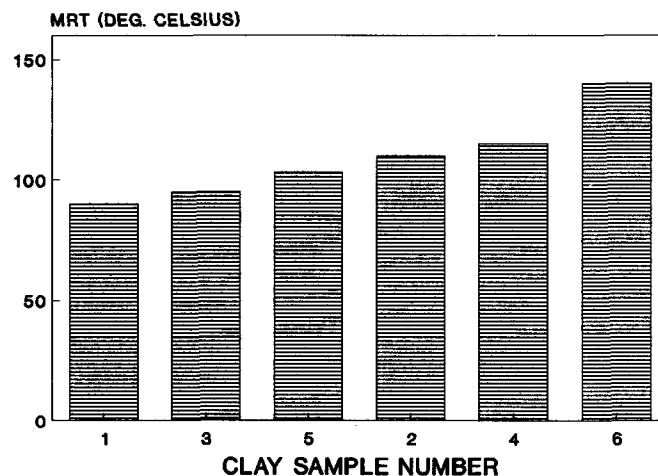


FIG. 9. Effect of clay type vs oil retention on minimum reaction temperature (CaTFISH test).

regarding the tendency of any particular clay to undergo spontaneous combustion when mixed with an oil. The data in Table 4 and corresponding bar graphs in Figure 9 can be used to illustrate the point. The data were obtained using the CaTFISH test to determine the relative reactivity of a series of commercially available bleaching clays when mixed with soybean oil under two different sets of conditions: i) 50% retention, clay and oil were mixed such that 50% oil retention was achieved or; ii) intrinsic oil retention, excess oil was briefly mixed with the clay, and then the clay/oil mixtures were filtered using a pressure filter at 85 lb/in². In the latter case, the oil retention obtained for each particular clay was intrinsic for the filtration conditions employed. Other filtration conditions might give different intrinsic oil retention values.

When the MRT's of clay/oil mixtures are measured at 50% oil retention, and arranged in ascending order (top graph, Fig. 9), clay 1 (a raw attapulgite) is the most pyrophoric and clay 6 (an acid-activated montmorillonite) the least. However, as shown by the data in Table 4, the

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TABLE 4

Minimum Reaction Temperatures of Some Commercial Bleaching Clays vs Level of Oil Retention

Clay sample no.	Clay type ^a	Intrinsic oil retention ^b (wt%)	MRT @ intrinsic retention (°C)	MRT @ 50% oil retention (°C)
1	RA	59.7	90	70
2	AM	64.9	110	95
3	AM	66.4	95	110
4	AM	52.6	115	115
5	AM	68.0	103	125
6	AM	38.4	140	155

^aClay type: AM, acid activated montmorillonite; RA, raw attapulgite.

^bIntrinsic oil retention = (wt of oil/wt of clay) × 100.

intrinsic oil retention properties of these clays vary considerably, and are seldom close to the 50% level. Furthermore, when the clay/oil mixtures are prepared at their intrinsic oil retention levels and then subjected to the CaTFISH test, it can be seen (bottom graph, Fig. 9) that the order of clay reactivity is changed, and that the range of MRT values is compressed. At 50% oil retention, the ranking in order of decreasing pyrophorosity is 1>2>3>4>5>6; at intrinsic oil retention levels, it becomes 1>3>5>2>4>6. Thus, while clay 1 (a raw attapulgite) maintains its #1 ranking as the most pyrophoric clay, and clay #6 (an acid-activated montmorillonite) is still the least pyrophoric, intermediate clays (all acid-activated montmorillonites) change order depending on the conditions under which their reactivity is measured.

Clearly, what these results point out is that any studies employing the CaTFISH test should utilize sample preparations which approximate actual conditions as closely as possible if the data from such studies are to be applied to any real world situations.

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