A Laboratory Study of the Press Effect in Adsorptive Bleaching[1]

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The so-called press effect is widely credited with enhancing the overall efficiency of bleaching clays in commercial operations. Laboratory bleaches are generally done with one use of bleaching clay, while plant operations often include a process in which spent clay in a filter press acts as a fixed bed to remove additional impurities from slurry-treated oil. In this study, the press effect is simulated in the laboratory by measuring the influence of a progressively-built filter cake on concentrations of carotenes and chlorophyll in successive batches of slurry-contacted oils. The oil used was canola; the clay tested was a commercially available acid-activated clay classified to two different average particle sizes. Conditions were chosen to simulate those used in commercial operations. Better total bleaching was seen from the first batch to the last as filter cake was built up. In addition, a significant particle size effect was seen.

KEY WORDS: Acid-activated clay, adsorption equilibrium, bleaching, canola oil, color removal, filter press, filtration, fixed bed, press effect, pressure drop.

The process called bleaching with acid-activated clays in the edible-oil industry is generally thought to be a combination of catalytic action (*e.g.*, peroxide destruction) and equilibrium adsorption (*e.g.*, pigment removal from the oil). In the experiments to be discussed here, we have focused on the latter phenomenon and specifically on the role of the activated clay or bleaching earth.

In Norris' chapter in Bailey's (1), quantitation of the equilibrium phenomenon with the Freundlich equation is discussed. This concept has also been described by Maza (2). Impurities in the oil, such as carotenes or chlorophyll, are attracted to the acid sites in the bleaching earth and adhere to the surface of the clay in an equilibrium fashion. These impurities are then effectively removed from the oil when the clay is filtered out.

This present work will describe a series of laboratory experiments designed to use the principles of adsorption equilibrium to demonstrate the press effect. This phenomenon, which has been mentioned (but not developed) in a number of publications (1,3,4) is often seen in commercial bleaching operations if the conditions are right.

Ordinarily, bleaching earths are tested in the laboratory by simulating commercial conditions as much as possible. While many plants operate in a continuous mode, the simplest way to compare bleaching clays in the laboratory is to heat the oil with a clay in a batch reactor, cool and filter. Color comparisons and constituent analyses allow the researcher to compare one clay with another or one set of process conditions with another.

While this procedure does furnish valuable, and most often adequate, information, there is another consideration worth noting. The continuous operation in a plant, or even a series of batch filtrations in a plant, can result in a substantial cake building up on the filter cloth. The term "press effect" refers to the observation that there is additional bleaching that can take place in this press cake. In terms of unit operations, the filter press cake acts as a fixed-bed adsorption "column." If the "spent" clay has additional capacity, that is, is not at total equilibrium with the oil it comes in contact with, this not-totally-spent clay can continue to remove impurities from the oil.

For that fixed bed to pick up extra impurities during the filtration step, whether of the original batch or of a separate batch, there must be some driving force for the impurities. If the clay is in equilibrium with the oil, no more net adsorption will take place and there will be no "press effect." If, on the other hand, the oil has not reached equilibrium with the bleaching earth in the cake, additional bleaching can possibly take place. Several experiments have been run to observe the effects of these nonequilibrium conditions.

EXPERIMENTAL PROCEDURES

Materials. The oil used was a refined but unbleached canola oil obtained in March 1992 from CanAmera Foods. A sample of acid-activated bleaching clay was obtained from Engelhard's Jackson, Mississippi, plant representing recent production.

The clay was first classified to have two different physical situations to work with. Clay L has the larger average particle size (36 microns); Clay S has the smaller average particle size (21 microns) (Fig. 1).

Two unit operations were involved in generating the present data—bleaching and filtration.

Bleaching equipment. The contacts were carried out in a modified resin kettle of the O-ring seal type. Ports at the top of the vessel provided for heating (through a metal coil immersed in the oil), temperature measurement (*via* thermocouple) and the application of atmospheric or vacuum conditions in the vessel. The heating coil and thermocouple were connected to a heater-temperature controller unit (Eurotherm brand), which was preset to the

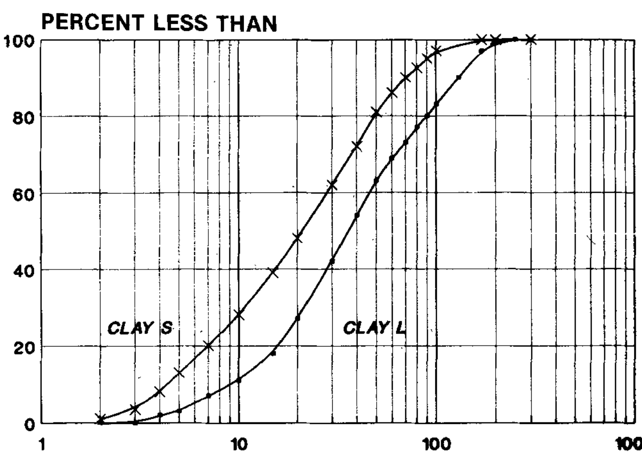

FIG. 1. Particle size distributions of two fractions of acid-activated clay: Clay S (—x—) and Clay L (—·—).

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desired temperature and gave consistent heat-up time, hold time and temperature from run to run. Vacuum of 27–28 in. Hg was provided by a vacuum pump.

Bleaching procedure. The desired amount of adsorbent was added to 150 g of oil (for Buchner filtrations) or 100 g of oil (for Gelman filtrations) at room temperature. After placing the magnetic stirring bar in the mixture, the lower part of the vessel was connected to the top. A metal collar was added to provide for a tight seal around the O-ring.

Evacuation of the vessel, agitation and heating commenced at about the same time. After the desired temperature was reached and the hold time was completed, the vacuum was released with nitrogen. The oil was cooled rapidly for the untimed filtrations in the Buchner funnel, but transferred hot in the experiments simulating a filter press with the Gelman filter described below.

Filtration equipment. Two types of filtration equipment were used. An 11-cm Buchner funnel (Coors Ceramics, Golden, CO) fitted with No. 2 Whatman paper was used in the preliminary experiments to determine the effect of clay dosage, hold time and temperature on color removal. A 200-mL capacity Gelman filter (Gelman Science, Inc., Ann Arbor, MI), model 4280, was used in the later experiments to do multiple-batch filtrations. For the filter-press simulation experiments, the Gelman filter was fitted with a 47-mm Teflon Millipore SM 5-micron cloth (Milford, MA) (Fig. 2).

Filtration procedure. As stated above, the oil was cooled rapidly before filtering with the Buchner funnel. Vacuum was provided by the house vacuum.

For the Gelman experiments, the filter was kept hot with a Master heat gun (Master Appliance Corp., Racine, WI). Oil was transferred hot after purging with nitrogen to minimize oxidation, and the top was secured on the Gelman. At time zero, 20-psig pressure was applied with nitrogen. The filtration was timed from the application of pressure to the breakthrough of nitrogen. The temperature of the oil was measured by a thermometer as it was discharged. Filtration was done at the contact temperature.

For the multiple-cake experiments, the Gelman filter was kept closed until it was needed for the next service. The cake build-up was not so extensive that it interfered significantly with the free volume of the filter cyclinder.

Analysis. The bleached and filtered oil was cooled and the colors [Lovibond red and ppb (ppb = 10^{-9}) chlorophyll] were read on a McCloskey Edible Oil Colorimeter.

RESULTS AND DISCUSSION

Standard conditions were established in the experiments described below to be 2% clay dosage, 20-min hold time at 27 in Hg vacuum and 248°F. As stated earlier, experimental conditions were desired in which a nonequilibrium situation was present at the end of a bleach run so that there might be a chance for additional bleaching to take place in the press cake during filtration. Several ways to achieve this were tested.

Particle size. Dosage is defined as the grams of clay contacted with 100 g of refined oil. If that clay is mostly small particles with a large amount of external surface area, the impurities can rapidly diffuse into the particles and contact most of the active sites. However, if the particles are large, more time is needed for this to take place.

Shortage of time. Adsorption is controlled by both equilibrium and kinetic factors. While the driving force for adsorption is the clay's capacity to hold impurities on its active sites, the impurities must have time to diffuse through the pores of the clay to reach the adsorption sites.

Shortage of clay. The addition of an overabundance of clay could effect the removal of virtually all of the impurities. However, that is almost never economical, and a compromise is reached in commercial practice in which a minimum amount (and dollar value) of clay is added to the oil to achieve acceptable quality.

Experiment No. 1—determination of the effect of bleach temperature on color removal. While laboratory bleaches of canola oil are often done at 248°F, some lower hold temperatures were also investigated. Figure 3 shows that the carotenes are effectively removed from canola oil with 2% of either clay, although not as completely with only a 6-min hold. However, the chlorophyll removal appears to be much more sensitive than carotenes to particle size, temperature and contact time (Fig. 4).

Experiment No. 2—determination of the effect of bleach time on color removal. To set standard conditions for the set of experiments examining the press effect, it was necessary to differentiate between equilibrium conditions

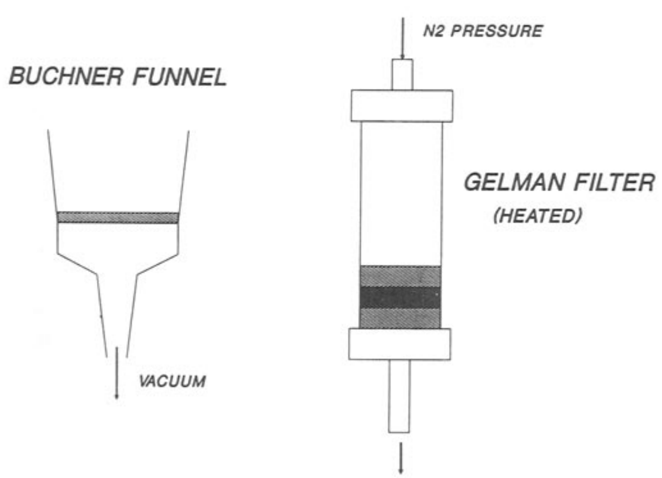

FIG. 2. Filters used in the laboratory for single-batch filtrations (Buchner funnel) or multiple filtrations (heated Gelman pressure filter).

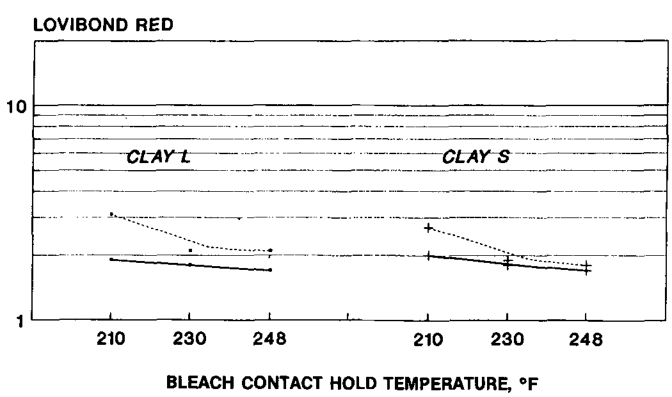

FIG. 3. Lovibond Red color after filtration as a function of batch temperature and hold time: Clay L for 6 min (– – • – –); Clay L for 20 min (— • —); Clay S for 6 min (– – + – –); Clay S for 20 min (— + —).

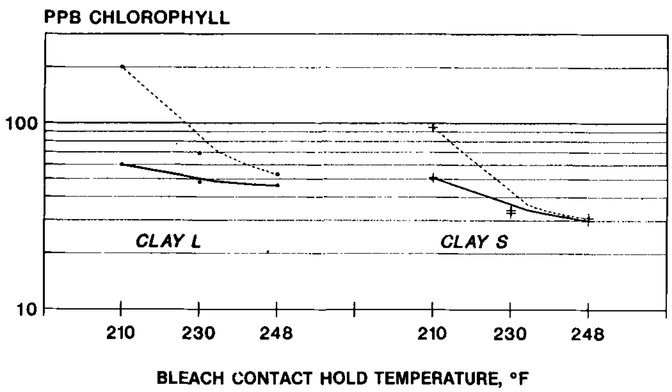

FIG. 4. Parts per billion (ppb) chlorophyll after filtration as a function of batch temperature and hold time. Clay L for 6 min (- - • - -); Clay L for 20 min (— • —); Clay S for 6 min (- - + - -); Clay S for 20 min (— + —).

and those where kinetics still govern the bleaching. The clay with the large average particle size, Clay L, was chosen to make the color *vs.* time comparisons. Those relationships are shown in Figures 5 and 6. It appears, first of all, that at 1.5% dosage, equilibrium is not reached in 30 min of holding after the batch reaches temperature. It is suspected, however, that the continuing decrease in red color is due to heat bleaching. With 2% clay in the slurry, no further change in either color is seen after 20 min. This time and dosage were therefore chosen to represent "equilibrium" conditions with this clay.

Experiment No. 3—determination of the effect of particle size on color removal. Two classic curves are presented in Figures 7 and 8. These show quite clearly that at equilibrium conditions, Clay S, with the smaller particle size, is slightly more effective in removing both carotenes and chlorophyll. Although both of these clays were once part of one sample, this difference can be rationalized in a number of ways, *e.g.*, more external surface area or possibly more acidity on the smaller particles. Each of

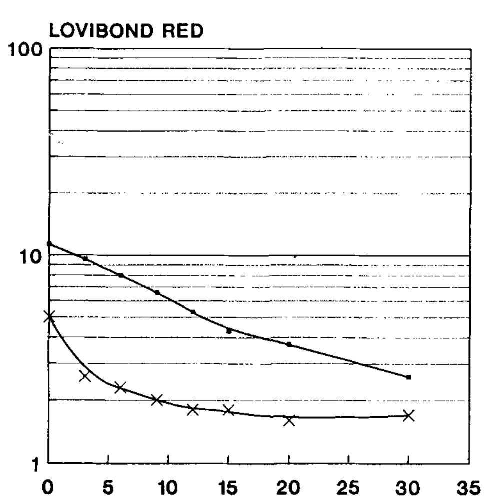

FIG. 5. Lovibond Red after filtration for Clay L: 1.5% clay dosage (— • —); 2.0% clay dosage (— x —). Heatup takes 10 min.

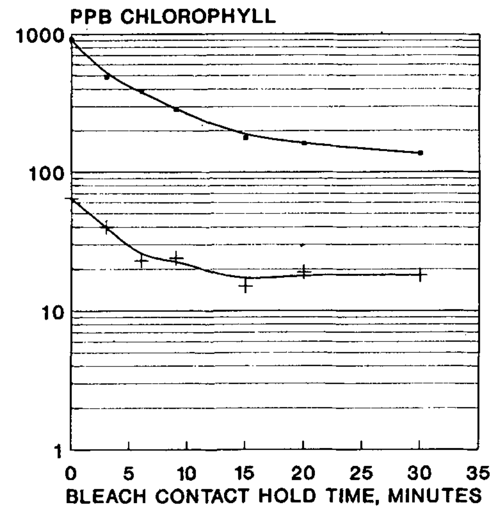

FIG. 6. Parts per billion (ppb) chlorophyll after filtration for Clay L: 1.5% clay dosage (— • —); 2.0% clay dosage (— x —). Heatup takes 10 min.

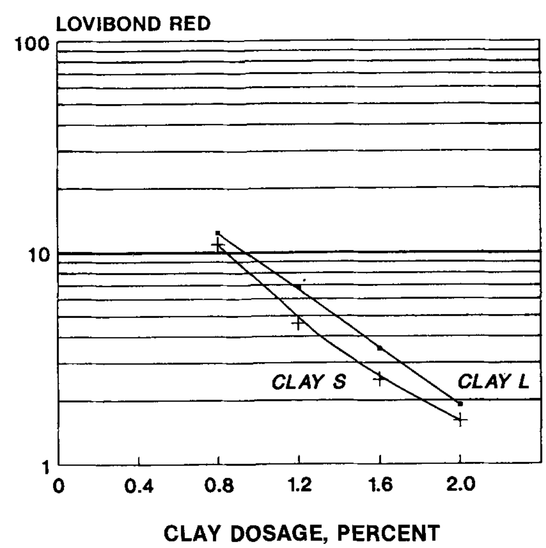

FIG. 7. Lovibond Red for each clay, single use. Clay L, (— • —); Clay S (— + —).

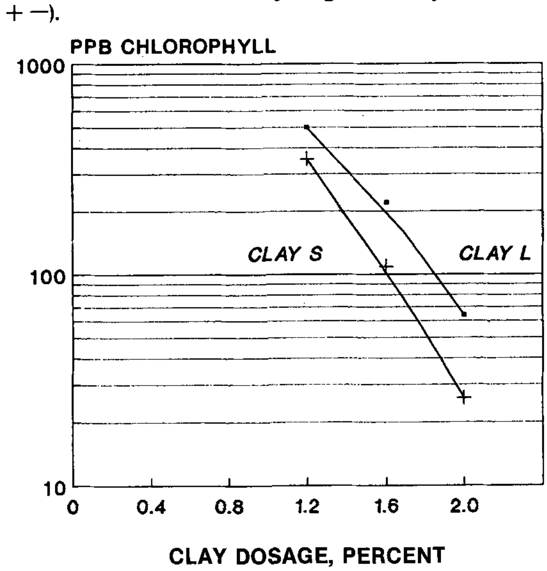

FIG. 8. Parts per billion (ppb) chlorophyll for each clay, single use. Clay L: (— • —). Clay S: (— + —).

the data points discussed so far was taken after a once-through filtration with the Buchner funnel.

Experiment No. 4—demonstrations of the press effect. The main objective can now be approached—performing multiple filtrations to show the press effect in oil bleaching. The previous Buchner-filtration data are used as the benchmark "ONCE THROUGH" data in Figures 9-12. The "CAKE BUILD-UP" points are the result of filtering successive bleached oil contacts through a fresh filter cloth on the Gelman filter for the first batch and then through the built-up cake for succeeding batches. For both clays, the first contact was done at 2% dosage and was filtered hot through the Gelman filter. The second contact was done at 1.6% dosage and filtered through the previous "2%" cake. The third contact at 1.2% and the fourth at 0.8% likewise were filtered through this cake. After four bleaches went through the filter, the cake was about 9 mm thick. This is, of course, much less than some cakes get in commercial operations, but it was enough to demonstrate the beneficial effect of filtering through a fixed bed of not-so-spent bleaching earth.

The difference between the solid line and the dashed line is the press effect. This effect was especially evident in the extra chlorophyll removal which took place in the filter.

The data for Clay S seems to be even more definitive than for Clay L.

A second set of experiments was run, in which, first, four 2% contacts were put through the same filter. Although the cake built up to 11 mm, there was little, if any, press effect noticed here (see the bottom lines in Fig. 13). Because the oil for all four batches was already in equilibrium with the cake, no press effect was expected. In an attempt to investigate a practice reported by several industry contacts, the dosage was next lowered in four successive contacts and filtrations. Starting with a 2% contact and filtration, the dosage was lowered in the next three contacts, and each was filtered successively through this same cake. Again, the color of the filtered oil was lower than it would have been had the filter been fresh (compare the middle curve in Fig. 13 with the dotted line connecting points taken from the single-filtration curves of Figs. 10 and 12). The programmed step-down of dosage

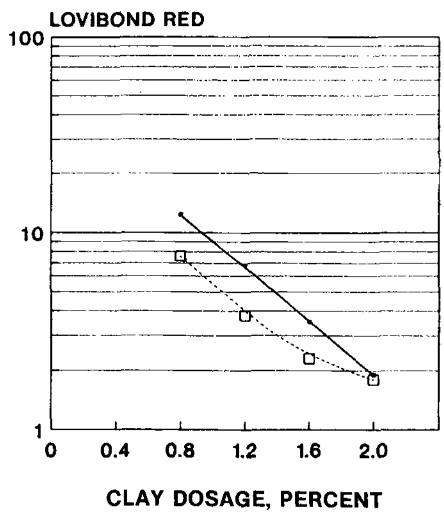

FIG. 9. Lovibond Red for Clay L, once through (— • —) or with cake build-up (- - □ - -).

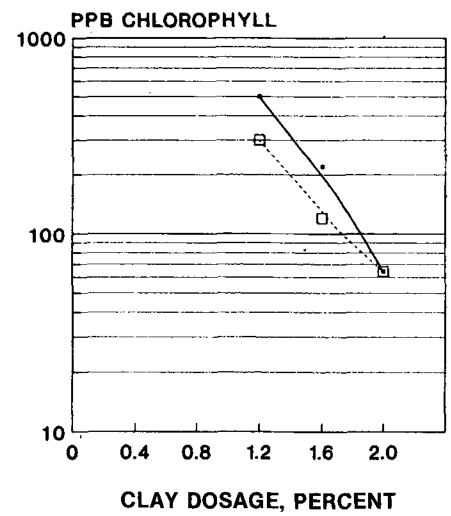

FIG. 11. Parts per billion (ppb) chlorophyll for Clay L, once through (— • —) or with cake build-up (- - □ - -).

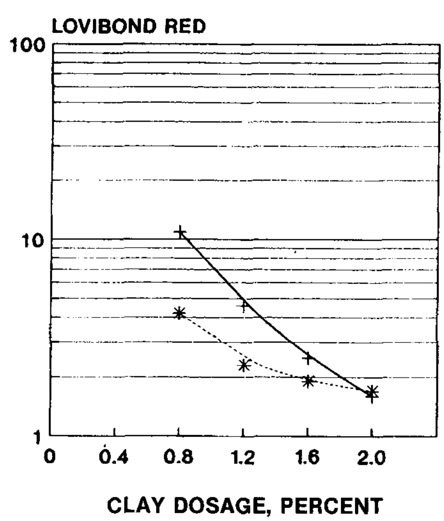

FIG. 10. Lovibond Red for Clay S, once through (— + —) or with cake build-up (- - * - -).

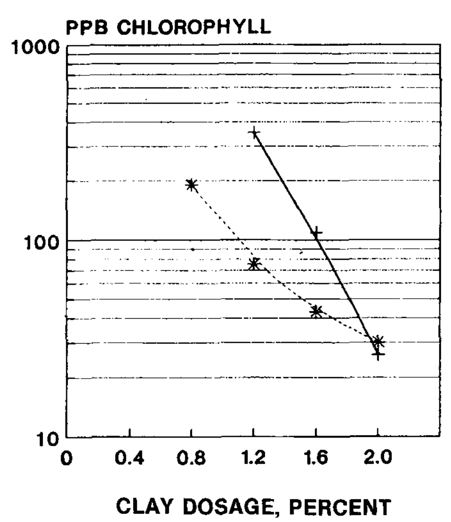

FIG. 12. Parts per billion (ppb) chlorophyll for Clay S, once through (— • —) or with cake build-up (- - * - -).

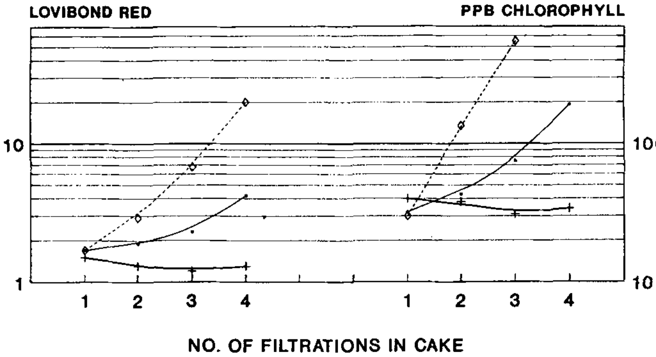

FIG. 13. Color for successive filtrations with Clay S: Successive dosages of 2, 2, 2 and 2% (— + —); successive dosages of 2, 1.5, 1 and 0.5% (— • —); corresponding equilibrium values at 2, 1.5, 1 or 0.5% (- - ◊ - -).

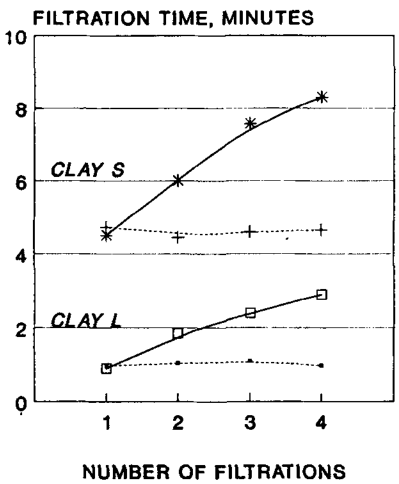

FIG. 14. Filtration time on the Gelman filter at constant pressure: Clay S, duplicates at 2% dosage (- - + - -); Clay S, "series" (— * —); Clay L, duplicates at 2% dosage (- - • - -); Clay L, "series" (— □ —). Note: The "series" was 2%, then 1.5%, then 1% and finally 0.5% dosage.

in these laboratory experiments is obviously too large to be effectively compensated for by the cake generated. However, the application of the press effect principle is evident.

Filtration data. Each successive batch filtered through the same cake had a longer processing time, as evidenced in Figure 14. To establish a base line, four batches were each filtered over a fresh filter. Then the times for each of the four successive batches mentioned in the previous paragraph were plotted. It is obvious that the filtration time increased considerably with each succeeding batch. In some commercial operations, this increase in filtration time could be a hindrance to trying to derive a benefit from the press effect; in others it might not. Where the pressure drop or the filtration time is a limitation, there still might be a case for successive filtrations if a faster-filtering clay (such as Clay L) is used.

The experiments described above lead to the following conclusions. (i) Clay contact times of 20 min or longer are necessary to achieve equilibrium bleaching of color bodies in laboratory contacts with canola oil; (ii) Clays with smaller average particle size have a bleaching advantage over the same clays with larger particle size; (iii) Successive filtrations through a filter cloth/cake can take advantage of underutilized clay in effecting an extra measure of color removal; (iv) The press effect can be beneficial but may be limited by filter rate or pressure drop considerations.

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