Adsorption of β-Carotene: II. On Cation Exchanged Bleaching Clays[1]

K.Y. LIEW, S.H. TAN, F. MORSINGH and **L.E. KHOO**, School of Chemical Sciences,
Universiti Sains Malaysia, Penang, Malaysia.

ABSTRACT

X-ray diffraction patterns of a number of commercial bleaching earths indicate that they consist mainly of montmorillonite mixed with smaller amount of kaolinites as well as mica, quartz and cristobalite. The active sites in these earths for the adsorption of β-carotene are identified through ion exchange and found to be the protonic sites and some metallic ions. The efficiencies of the various cations in imparting activities to the earths are found to be in the order $Mg^{2+} > Fe^{3+} > H^+ > Ca^{2+} > Na^+$. For Fe^{3+} and H^+ exchanged clays, the activity was found to be linear function of the concentration of these ions. The high activities of Mg^{2+} and Ca^{2+} exchanged clays are discussed.

INTRODUCTION

It is well known that bentonites in their natural state have limited ability to bleach coloring materials during industrial bleaching of vegetable fats and oils. To improve on the bleaching property, the commercial clays are usually acid-activated (1). Recently, the moisture content of bleaching earths has also been reported to be an important factor for the bleaching of palm oil and other vegetable oils (2-4). Although there are reports that ferric ions interact with β-carotene (5,6) and copper ions deteriorate the quality of palm oil (7), the role of metallic ions in bleaching has not been well investigated (8). We carried out a study on the effect of metallic cations on commercial cation exchanged bleaching earths with respect to the adsorption of β-carotene and are reporting the finding.

EXPERIMENTAL

The β-carotene used was obtained from BDH Chemicals Ltd., England, and was recyrstallized from methanol/chloroform mixture. The recrystallized substance was dried and stored in a darkened vacuum desiccator. All solvents used were analar grade and were dried with activated molecular sieve 3A before use. Acid-activated clays, i.e., Filtrol 105, Fulmont and Galleon V2, were gifts from Palmex and Magri Palm Oil Refineries, Penang, Malaysia. The clay samples were heated at 100 C overnight in an oven before ion exchange.

Na^+ exchanged clays were prepared by the following procedure. A weighed sample of the clay was stirred with distilled water for about 30 min at room temperature. The slurry was centrifuged and the supernatant solution was decanted and collected. The washing was repeated until a constant pH was obtained for the supernatant solution. The accumulated supernatant and washing solutions were analyzed for concentrations of H^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+} and Cu^{2+}. To 100 g of the washed and dried clay was added 200 mL of 1 M NaCl solution and this mixture was stirred at room temperature for 2-3 hr before the slurry was centrifuged. The supernatant solution was decanted and collected. The Na^+ exchanged clay was washed free of residual sodium salt. The accumulated supernatant and washing solutions were analyzed for the concentration of the various ions. The procedure was repeated for a second and a third time. The results are shown in Table I.

TABLE I

Concentrations of Various Cations Exchanged by Na^+ in Filtrol Clay

Filtrol samples	Concentration exchanged, x 10^{-2} meq g^{-1}				
	H^+	Mg^{2+}	Ca^{2+}	Fe^{3+}	Na^+
Water-washed	3.48	3.97	26.80	0.52	2.07
Once-exchanged	3.97	1.35	11.20	2.71	–
Twice-exchanged	7.39	2.28	17.05	4.32	–
Thrice-exchanged	10.45	2.95	19.60	5.34	–

Preparations of the H^+, Fe^{3+}, Mg^{2+} and Ca^{2+} exchanged clays were achieved as follows. Na-clay was equilibrated with solutions containing the appropriate cations at concentrations between 0.01 M and 0.03 M at room temperature for about 1 hr. The slurry was centrifuged and the supernatant solution was collected. The resulting clay was washed several times until it was free of any residual salt or acid. The exchanged clay was dried in an oven at 100 C overnight. The extent of exchange was determined by the analysis of the residue concentration of the cation and counter-checked by the amount of the sodium ions displaced.

All samples were heated to 450 C for 4 hr in air before adsorption experiments were done. The detailed procedures for obtaining the adsorption isotherms have been described (8).

X-ray diffraction patterns of the clays were recorded on a Philip Diffractometer using copper Kα radiation at 40 kV and 30 mA. The samples were scanned over a 2θ range of 5-35° at a speed of 1°/min. Surface areas were determined by the BET method at 77.4 K using nitrogen as the adsorbate. Surface acidities were determined by nonaqueous titration with *n*-butylamine as the titrant and triphenylmenthanol as the indicator (9).

RESULTS AND DISCUSSION

Structure

X-ray diffraction patterns show that the three commercial clays Filtrol, Fulmont and Galleon consist mainly of the

---

[1] Presented in part as paper T12 in the International Conference on Palm Oil Product Technologies in the Eighties, Kuala Lumpur, May 1981.

clay mineral montmorillonite (Fig. 1, a and b). In addition to small amounts of quartz and mica, Filtrol and Fulmont clays contain a substantial amount of kaolinite. A fair amount of α-cristobalite is found in Galleon. The crystal structure of the montmorillonite in these clays is not adversely affected by the various exchange processes and even when the clays were treated with 0.1 M sodium hydroxide (Fig. 1, c, d, e and f). After cation exchange and heating to 450 C, the 3.52 Å d spacing in Filtrol and Fulmont disappeared, indicating that the kaolinite mineral in these clays had become amorphous (10). When the montmorillonite clays were heated at 450 C for 4 hr, most of the interlayer water was removed and the original 001 spacing at 15-16 Å was replaced by one at 10-11 Å (Fig. 1).

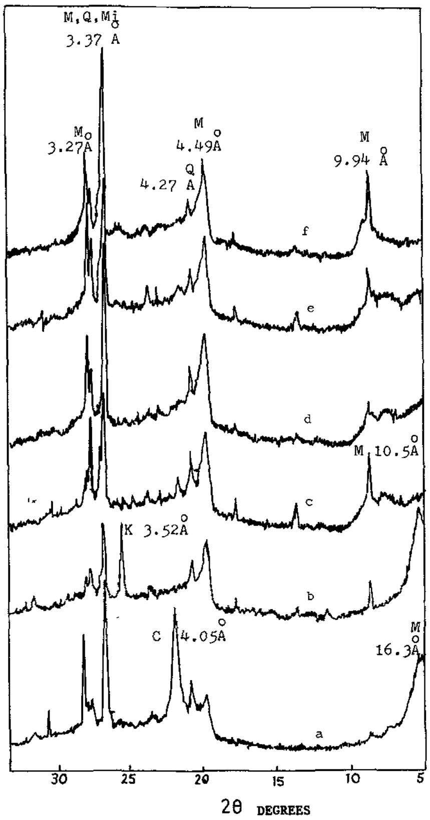


FIG. 1. X-ray powder diffractogram for (a) Galleon without heat treatment, (b) Filtrol without heat treatment (c) H^+ exchanged Filtrol (0.258 meq g^{-1}) heated at 450 C, (d) Mg^{2+} exchanged Filtrol (0.209 meq g^{-1}) heated at 450 C, (e) Fe^{3+} exchanged Filtrol (0.255 meq g^{-1}) heated at 450 C and (f) Filtrol treated with 0.1 M NaOH and heated at 450 C. (M, montmorillonite; Mi, mica; Q, quartz; K, kaolinite; C, cristobalite.)

The BET surface areas of the cation exchanged clays were determined after the clays were heated at 450 C in air for 4 hr. These areas are listed in Table II. It can be seen that the cation exchange processes do not appreciably affect the surface areas. The heat treatment resulted in the removal of interlayer water and this caused the collapse of the montmorillonite structure. The high external surface area for Filtrol (300 m^2g^{-1}) compared to that of the bentonite clays (50-100 m^2g^{-1}[11]) is due to the acid activation which caused the formation of a wide range of pores (1). That these pores are still present in the cation exchanged and heat-treated clays is indicated by the small change in the external surface area.

TABLE II

Surface Area and Acidity of Cation-Exchanged Filtrol Clays after Heat Theatment at 450 C

Samples	Extent of exchange (x 10^{-2}meq g^{-1})	*n*-Butyl-amine[a] titer (meq g^{-1})	Surface area (BET) (m^2g^{-1})
Original Filtrol	–	–	307
Washed Filtrol	–	0.12	–
Na-Filtrol	–	0.07	297
H-Filtrol	25.7	0.10	280
Fe-Filtrol	25.5	0.12	270
Mg-Filtrol	20.9	0.11	–
Ca-Filtrol	21.5	0.08	–

[a] Acidity determined using triphenylmethanol indicator (pK_{R^+} = -6.63).

ADSORPTION OF β-CAROTENE

When the β-carotene in acetone solution was stirred with activated Filtrol clay, the absorption intensity of the supernatant solution at λ_{max} =452 nm decreased sharply immediately. The clay which was originally creamy beige in color turned dark green. After about 5 min, the intensity at 452 nm increased slowly with time. This indicates that the original all-*trans* β-carotene initially was adsorbed very quickly, followed by a slow desorption of an adsorbed species which has very similar ultraviolet (UV)-visible absorption. This similarity, except for the poor resolution of the triplet in the visible region of 452 nm for the original β-carotene, indicates that the desorbed compound is probably an isomer of β-carotene. TLC analysis shows that only one compound, other than the original all-*trans* β-carotene was present at this early stage of the reaction. After 1 hr, it was found that, at temperatures of 20 and 30 C, ca. 27 and 17%, respectively, of the originally adsorbed carotene was desorbed.

The apparent adsorption isotherms for β-carotene by Filtrol, Fulmont and Galleon are shown in Figure 2. These are of the Langmuir type. The most active clay is Fulmont, followed by Filtrol and Galleon. At the supernatant concentration of 1.0 x 10^{-5} mole fraction, Galleon is four times less active than Fulmont and three times less active than Filtrol.

EFFECT OF CATION EXCHANGE WITH Na^+

Upon neutralizing the acidic Filtrol clay with 0.1 M NaOH solution, the adsorption activity was reduced from 3.5 x 10^{-6} to 0.7 x 10^{-6} mol g^{-1} at a supernatant concentration of 1.0 x 10^{-5} mole fraction (Fig. 3). The treatment of the clay with NaOH resulted in the neutralization of the acidic centers present on the surface and also in some exchange of the exchangeable cations with sodium ions. The decrease in activity is attributed largely to removal of the acidity as well as the removal of the exchangeable cations in the clay.

To verify the above, the Filtrol clay was water-washed until a constant pH was obtained. The washed clay was then equilibrated three times with 1.0 M NaCl solution to exchange the exchangeable cations with Na^+ ion. During the washing, H^+, Na^+, Mg^{2+}, Ca^{2+} and Fe^{3+} were leached out. The ions that were exchanged with Na^+ were H^+, Ca^{2+}, Mg^{2+} and Fe^{3+}. The concentrations of these ions are shown in Table I.

The adsorption isotherms of the washed, once-, twice- and thrice-exchanged samples are shown in Figure 3. As the cations were leached out or progressively exchanged for

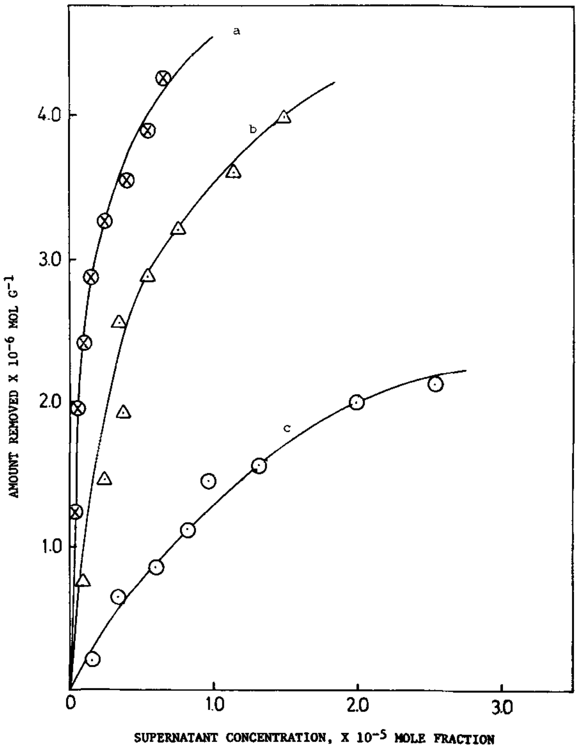


FIG. 2. Apparent adsorption isotherms for β-carotene by (a) Fulmont, (b) Filtrol and (c) Galleon, heated at 450 C.

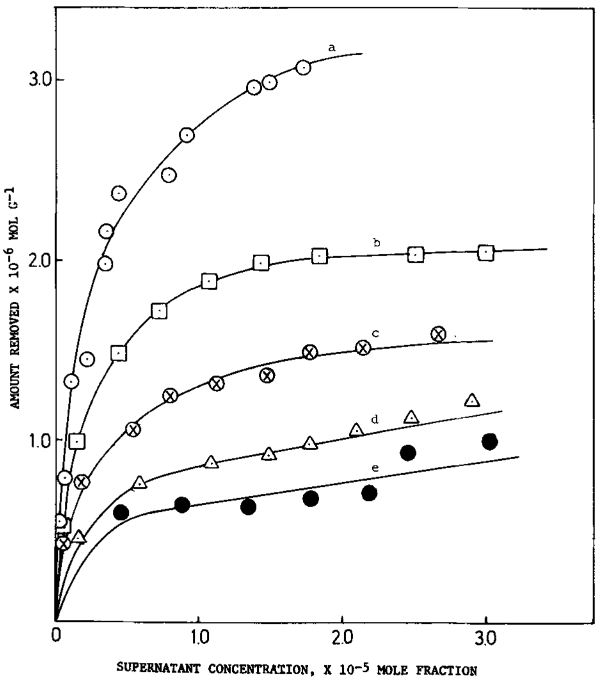


FIG. 3. Apparent adsorption isotherms for β-carotene at 25 C on Filtrol (a) washed, (b) once-exchanged with Na^+, (c) twice-exchanged with Na^+, (d) thrice-exchangedwith Na^+, (e) neutralized with 0.1 M NaOH, activated at 450 C.

Na^+ ions, the activity of the clay decreased. At a supernatant concentration of 1.0×10^{-5} mole fraction, the activity of the various samples were: washed, 2.8×10^{-6} mol g^{-1}, once-exchanged, 1.9×10^{-6} mol g^{-1}, twice-exchanged, 1.3×10^{-6} mol g^{-1} and thrice-exchanged, 0.9×10^{-6} mol g^{-1}. Washing of the Filtrol clay resulted in a large amount of cations, totaling 0.37 meq g^{-1} being leached out. Some of these ions, e.g., part of the H^+ ions, are physically adsorbed and hence washable, whereas other ions are constituent ions of the clay structure. These ions are leached out probably because of the internal rearrangement of the lattice by the action of the washings. This may have caused the decrease in activity. The decrease in activity after Na^+ ion exchange indicates that Na^+ ions have very little activity for adsorption of β-carotene.

ACTIVITY OF CATION EXCHANGED CLAYS

The activities of the various cation exchanged clays were investigated by exchanging the Na^+ ions in the thrice-Na^+ exchanged clays with H^+, Fe^{3+}, Mg^{2+} and Ca^{2+} ions. The apparent adsorption isotherms of these cation exchanged clays for β-carotene are shown in Figure 4, A, B and C, for Fulmont, Filtrol and Galleon, respectively. It is demonstrated that, for a comparable level of exchanges for Fulmont and Galleon, the activity of the various cation exchanged clays are in the order of $Mg^{2+} > Fe^{3+} > H^+ > Ca^{2+} > Na^+$. For Filtrol clay, Mg^{2+} exchanged samples seem to be less active than the Fe^{3+} exchanged sample at higher supernatant concentration.

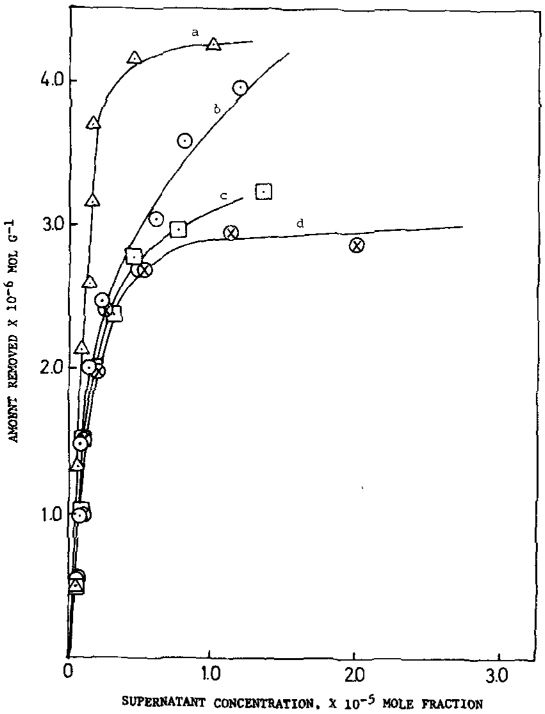
The activity of H^+ and Fe^{3+} exchanged filtrol was investigated with respect to the extent of exchange. A constant initial concentration of β-carotene was used. The results are shown in Figure 5. It is observed that the activity increases linearly with the extent of exchange for both cations. The gradients obtained are 0.82×10^{-2} mol g^{-1} and 1.19×10^{-2} mol g^{-1} for the H^+ and Fe^{3+} exchanged clays, respectively. The linear increase of activity with the extent of exchange indicates that the active sites involved are chemically equivalent at different extent of exchange.

The acidity of the various cation exchanged Filtrol was determined by nonaqueous titration with *n*-butylamine (Table II), These clays were washed until the pH of the washing was more than 6 so that the contribution from free acid is negligible. These values determine the amount of protonic sites on the clay surface which are accessible to the *n*-butylamine molecules. No direct correlation between the activity and acidity can be deduced. However, we can conclude that the more active samples generally have higher acidity than the less active samples.

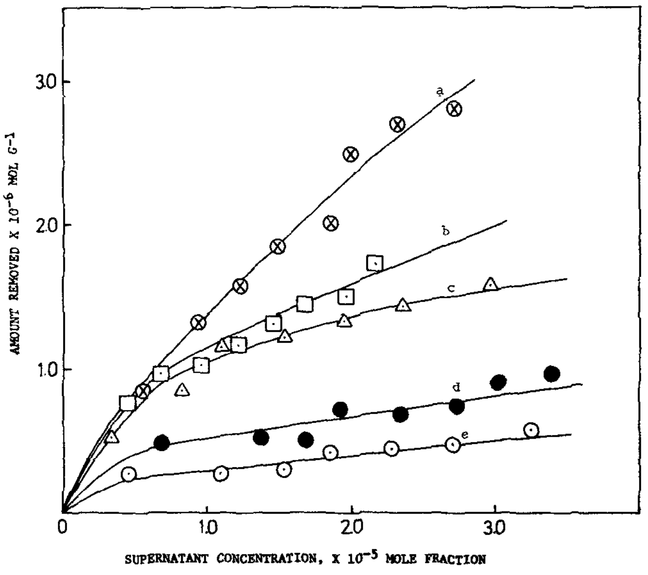
Metallic ions Fe^{3+}, Mg^{2+} and Ca^{2+} impart considerable activity to clays for β-carotene adsorption. It is suggested that the β-carotene molecules can either be adsorbed directly onto the cations to form a chemisorbed complex and then undergo further reactions or may interact directly with the protonic centers present on the clay surface. The first way is likely for transition metal ions such as Fe^{3+} (5,8). Interaction between alkaline earth cations with adsorbed molecules such as butene and pyridine have been observed (12). If the alkaline earth cations can interact with the β-carotene molecules, the activities of these cation exchanged clays may be expected to increase as the electrostatic fields due to these ions increase as their ionic radii decrease. Thus, Mg^{2+} exchanged clays are more active than Ca^{2+} exchanged clays. Alternatively, the presence of metallic ions on the surface may induce dissociation of chemisorbed water, resulting in the production of Bronsted centers such as $M^{2+}(OH_2) \rightarrow M(OH)^+ + H^+$ (13). It is likely that both reactions occur on the surfaces.

ACKNOWLEDGMENT

Financial support from Universiti Sains Malaysia and Palm Oil

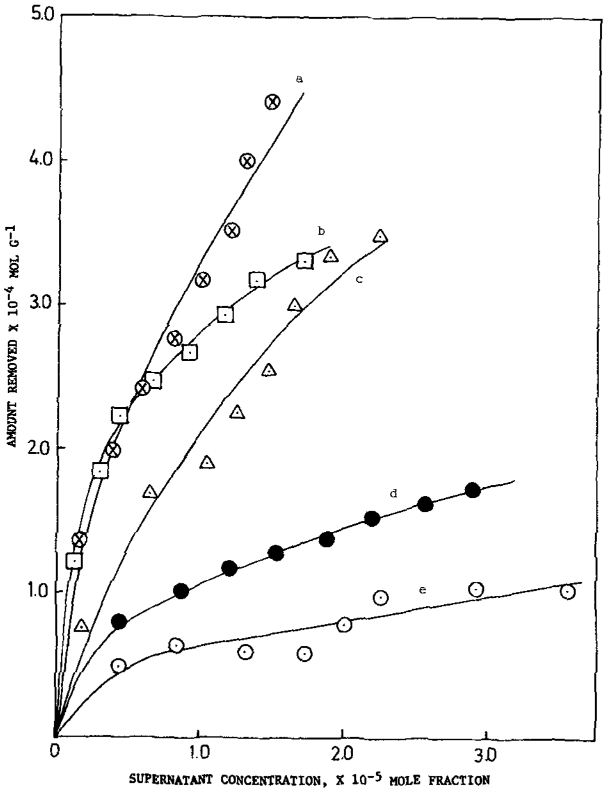


(A)



(C)

FIG. 4 (A). Apparent adsorption isotherms for β-carotene at 25 C by cation exchanged Filtrol (a) Mg^{2+} exchanged (0.259 meq g^{-1}), (b) H^+ exchanged (0.160 meq g^{-1}), (c) Fe^{3+} exchanged (0.136 meq g^{-1}) and (d) Ca^{2+} exchanged (0.261 meq g^{-1}), activated at 450 C. (B) Apparent adsorption isotherms for β-carotene at 25 C by cation exchanged Fulmont (a) Mg^{2+} exchanged (0.250 meq g^{-1}), (b) Fe^{3+} exchanged (0.243 meq g^{-1}), (c) H^+ exchanged (0.275 meq g^{-1}), (d) Ca^{2+} exchanged (0.228 meq g^{-1}) and (e) Na^+ exchanged, activated at 450 C. (C) Apparent adsorption isotherms for carotene at 25 C cation exchanged Galleon (a) Mg^{2+} exchanged (0.217 meq g^{-1}), (b) Fe^{3+} exchanged (0.230 meq g^{-1}), (c) H^+ exchanged (0.230 meq g^{-1}), (d) Ca^{2+} exchanged (0.209 meq g^{-1}) and (e) Na^+ exchanged, activated at 450 C.



(B)

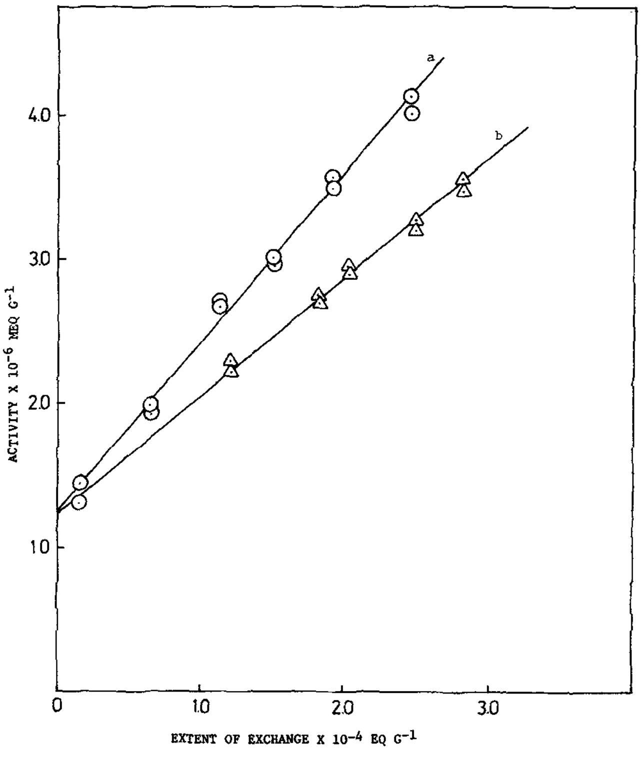


FIG. 5. Activity of cation exchanged Filtrol for adsorption of carotene at 25 C as a function of the extent of exchange of Na^+ with (a) Fe^{3+} and (b) H^+. The adsorbents were heated at 450 C.

Research Institute of Malaysia is acknowledged.

REFERENCES

1. Grim, R.E., Applied Mineralogy, McGraw-Hill, New York, NY, 1962, pp. 322, 313.
2. Zschau, W., Bleaching of Palm Oil, Palm Oil Product Technologies in the Eighties Conference, Kuala Lumpur, Malaysia, 1981, paper TP3.
3. Brimberg, V.U.I., Fette Seifen Anstrichm. 83:184 (1981).
4. Rich, A.D., JAOCS 44:298A (1967).
5. Bruggemann, J., W. Krauss and J. Tiews, Naturwissenschaften 38:562 (1951).
6. Savinov, B.G., and A.A. Svishehuk, Ikr. Khim. Zhr 16:57 (1950).
7. Shaw, D.B., and G.K. Tribe, Use of Activated Earths in Palm Oil Refining and Their Effects on Trace Metals Contaminants, Palm Oil Product Technologies in the Eighties Conference, Kuala Lumpur, Malaysia, 1981, paper TP5.
8. Khoo, L.E., F. Morsingh and K.Y. Liew, JAOCS 56:672 (1979).
9. Hirschler, A.E., J. Catal. 2:428 (1963).
10. Carrol, D., Clay Minerals: A Guide to Their X-ray Identification, The Geology Soc. of America, 1974, special paper 126, USA.
11. Van Olphen, H., Proc. of Intern. Symp. on Surface Area Determination, Butterworths, London, 1969, p. 225.
12. Ward, J.W., J. Catal. 11:259 (1968).
13. Ward, J.W., Ibid. 10:34 (1968).

[Received February 1, 1982]

Comparative Efficiencies of Bread Crumb Softeners at Varied Bread Storage Temperatures

K. LORENZ and **W. DILSAVER**, Department of Food Science and Nutrition, Colorado State University, Fort Collins, CO 80523 and **K. KULP**, American Institute of Baking, 1213 Bakers Way, Manhattan, KS 66502

ABSTRACT

A series of commercial surfactants was evaluated in white pan bread for their crumb antifirming effects during storage at 10, 20, 30, 40 and 50 C. These agents produced softer breads at all temperatures as compared to bread without surfactants. Although breads kept at 40 and 50 C remained softer than at room temperature (25 C), storage at elevated temperatures is not advised due to possible organoleptic and microbial deteriorations. At temperatures below 25 C, faster firming generally occurred, but was much less in the presence of surfactants. This observation suggests that a surfactant system might be found to retard firming at those conditions.

INTRODUCTION

Many concurrent changes take place in bread during storage; all are part of a complex phenomenon—generally called "staling." Specificially, as bread ages, we observe crumb firming, detect an increasing degree of crumb-texture harshness, loss of crust crispness, and also disappearance of fresh bread flavor concurrent with emergence of stale bread flavor (1). Although all these factors contribute to reduction of freshness and thus to a decrease of consumer acceptability of the product, the changes in firmness are given a preeminent importance in evaluation of staleness because they are readily detectable by the consumer; they are also correlated with organoleptic deterioration of organoleptic properties of breads during early stages of storage (2).

It is generally accepted that retrogradation of starch polymers is responsible for firmness characteristics of breads —amylose for the firmness of freshly baked bread and amylopectin for the progressive firming during bread storage (3). Retrogradation is essentially a crystallization process, involving transformation of amorphous starch into an ordered crystalline state. As expected for this type of reaction, it proceeds at a rate with a negative temperature coefficient. This was shown by Cornford et al. (2) for bread. Complexation of amylose with surfactants also lowers the swelling power of starch granules, making more water available for the gluten phase. This effect may indirectly influence moisture distribution between starch and gluten phases in bread (3,4) and reduce the crumb firming rate. The practical consequences of this trend are that breads firm more quickly as the storage temperature decreases; consequently, it is advisable to keep breads at room temperature rather than in a refrigerator.

To maintain bread softness for a longer period of time, the baking industry generally uses various surfactants that are permitted by FDA Standards of Indentity (5). The antifirming characteristics of these agents are attributed to their abilities to form insoluble helical complexes with amylose, to interact to a limited extent with amylopectin, and also to strengthen doughs by complexation with proteins (6-9). The effectiveness of surfactants varies in these interactions, as was shown by various investigators.

In basic research studies, effects of bread storage temperature on bread firming rates have been determined in the absence of surfactants. Practical evaluation of surfactants in bakery foods were usually limited to room temperature, since breads are generally kept at that temperature in plants, supermarkets and homes.

In the present study, we examined and compared the softening effectiveness of surfactants over the temperature range of 10-50 C to provide information for predicting firmness changes at various temperatures, and also, to determine if any of the selected surfactants might aid in maintaining bread softness in the refrigerator (an effect which would be advantageous since flavor and microbial deteriorations would also be retarded).

MATERIALS AND METHODS

Baking Procedure