Interaction of Fat-Containing Food with Plastics Packaging[1]

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ABSTRACT

Packagings for fatty food should protect against light, oxygen, microorganisms, and loss of water vapor and flavor substances. Low off-taste and adequate mechanical stability is required. Pigmented plastics fulfill most of these requirements. Two main effects caused by the interaction of fatty food components with plastic packaging materials are described: stress cracking and migration. A method for characterizing fatty foodstuffs was developed to distinguish between foodstuffs containing free fat available on the surface and those actually having an aqueous surface. The basic types of migration behavior are shown by typical migration curves of an antioxidant from rigid PVC and from HD-PE into test fat. In model experiments, the swelling of the HD-PE as well as the migration of the antioxidant was determined quantitatively as a function of time by means of radiotracer techniques. Based on these results and Fick's diffusion equations, a theory was developed with which it is possible to describe the migration behavior of antioxidants from polyolefins and PVC quite precisely. It was also possible to solve some problems with HI-PS. This mathematical model permits calculation of the migration at constant temperature as a function of time and concentration of the antioxidant in the polymer. As there is a definite mathematical relationship between the concentration of an additive in the polymer and the migration into test food or actual food, it is recommended that regulations for plastic food packaging are based on compositional limits, rather than migration limits, because of definite advantages in compliance and control.

REQUIREMENTS FOR PACKAGING FATTY FOODS

The aim of selecting packages is to find those which provide the necessary protection of the product at minimal cost. There are some requirements for plastic packages used for the packaging of fatty food. Fatty food normally needs a certain protection from light and, if this is not possible, from the influence of oxygen. The material should further hinder the penetration of microorganisms which might deteriorate the product. For emulsions, the packaging material should avoid the loss of water vapor and for dry powders, e.g., instant soups, it should avoid water uptake. In special cases it may be necessary to have a packaging material which is nearly impermeable to flavor substances.

Some of the relevant properties of packaging materials are compiled in Table I. With respect to the protection from water vapor loss or uptake, polyethylene (PE) or polypropylene (PP) are excellent, whereas polyvinylchloride (PVC) in most cases is still sufficient. However, the oxygen-permeabilities of all materials except PVC are high. Therefore, sufficient light protection is normally needed. In order to obtain this with the mass polymers, pigments are added. The exception is an alu/board/plastic laminate which has excellent light protection per se. Other demands are low off-taste from packaging material and adequate stiffness. Here, again, PVC has definite advantages.

INTERACTION BETWEEN FOOD COMPONENTS AND PACKAGING MATERIAL

Obviously the packaging material must retain its desired properties, even in contact with fatty food, i.e., the interaction with food components should be little. There are two main interaction effects: stress cracking and migration.

Stress Cracking Effects

In case of high impact polystyrene (HI-PS) an interaction with fat may become so intense that, under additional influence of stress the containers may suffer from stress cracking. This situation is given during transport and storage on pallets, where the lowest layer of containers often have to permanently resist the stress of all the upper layers. Figure 1 (results from W. Rabel, Hamburg) shows some cracking curves of PS-films, loaded with 1900 p. The time is plotted on the abscissa and the cumulative frequency of cracking on the ordinate, as stress cracking is a statistically occurring process. A material can be well characterized by the time necessary for 50% of the samples to stress crack. Under practical conditions, a stress cracking rate of more than 0.1% would not be tolerated. As shown in Figure 1, Ceres margarine, which is made of medium-chain triglycerides, has a strong tendency to cause stress cracking (curve no. 2), as after 4 min, 50% of the samples are already broken. Sunflower oil and butterfat have the same stress cracking activity (curves nos. 3 and 4), whereas butter as an emulsion is a little less active than butterfat. Fine

TABLE I

Properties of Packaging Materials

	Polyethylene high density	Polypropylene	Polyvinyl chloride	Alu/board/ plastic-laminate	High impact polystyrene
Light tightness	By pigments	By pigments	By pigments	Excellent	By pigments
Water vapor[a]	0.8	1.4	8.3	Variable	∿310
Oxygen[b]	85	58	4	High	∿140
Off-taste	Occasional	Rare	No	Rare	Rare[c]
Elasticity modulus[d]	9	11	33		∿30

[a] $\times 10^9$ [$gcm^{-1}h^{-1}Torr^{-1}$].
[b] $\times 10^{10}$ [$cm^2s^{-1}at^{-1}$].
[c] if styrene content high.
[d] $\times 10^{-4}$ [Ncm^{-2}].

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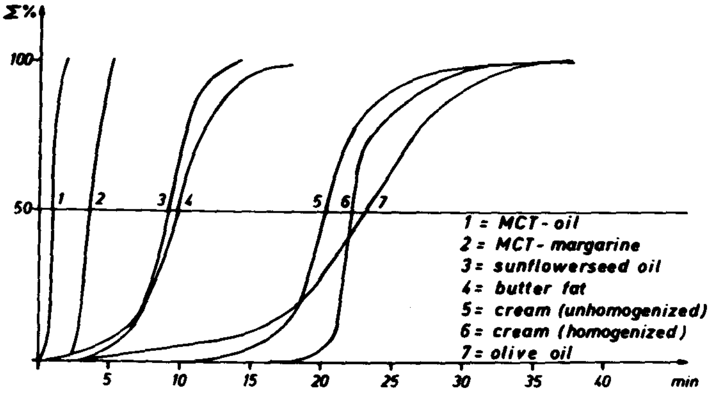

FIG. 1. Stress cracking curve of PS. Load: 1900 p.

emulsions as in SB margarine are definitely less active than the parent sunflower oil. It is the same for cream (curve nos. 5 and 6), which has butterfat as active ingredient. Quite an unusual curve is found for olive oil (curve no. 7), where stress cracks are found very early, but it takes quite a long time to reach the 50% value. Stress cracking always means that there is a definite interaction with a food component, e.g., fat. But, it cannot be concluded that there is no interaction if there is no stress cracking.

Characterization of Fatty Food

Before discussing the main interaction effect, i.e., the transfer of packaging ingredients into the food, it may be advisable to reflect on the meaning of fatty food. With respect to interaction, food should be considered fatty food if free fat is available on the surface and this type of food should be clearly distinguished from other fat-containing foods which actually have an aqueous surface, possibly containing some protein and carbohydrate. Koch and Figge (1) developed a relatively simple test to characterize food by bringing the food into contact with a low density polyethylene (LD-PE) film under standard conditions (Fig. 2). After separation of the film, one either determines the amount of fat taken up by the LD-PE film or the migration of an additive soluble in fat but not in water, e.g., an antioxidant, which can be easily determined in food.

The results of such investigations are compiled in Table II. At the bottom is the behavior of water, which shows an apparent fat transfer of 20 μg to the PE film and a very small uptake of antioxidant. With respect to migration, the group up to processed cheese can be considered aqueous, because the transfer of antioxidant remains very little, although the fat content of the processed cheese is 26% or for coffee creamer 10%. All the foods which show a migration of more than 100 μg of antioxidant should be considered as definitely fatty. This migration value corresponds—with exception of olive oil—to about 2,000 μg of uptake of fat into the PE. In between, there is a group of foods which show migration values of ca. 50 μg antioxidant and an uptake of fat between 1,000 and 2,000 μg by the PE. These foods show a definitely reduced uptake of migrants from packaging material, although they may contain up to 80% of fat like mayonnaise, which, however, is an oil-in-water emulsion.

The advantage of having PE as test film is that the character of food is not affected during the test because the loss of water vapor remains small, corresponding to the behavior of a good packaging material.

Further on in this paper, fatty food is defined as food which takes up more than 100 μg of antioxidant under the test conditions.

Migration of Packaging Additives into Fatty Food or Test Fat

Typical migration curves are shown in Figures 3 and 4. The behavior of a packaging material like rigid PVC with practically no interaction with the fat, e.g., sunflower oil and, at the same time, practically no migration of the additive—an antioxidant—within 60 days is given in Figure 3. At the beginning, the antioxidant is washed off from the surface and then we have hardly any increase in concentration. The curve is completely different with the same triglyceride and antioxidant but HD-PE as polymeric matrix. In this case, the fat is able to swell the PE and thus

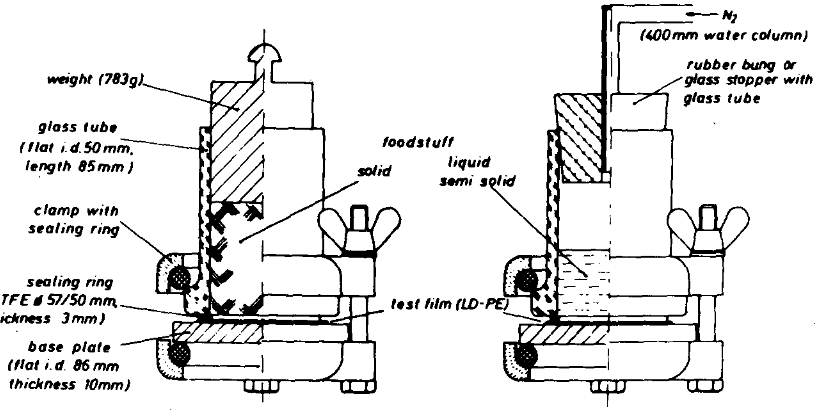

FIG. 2. Test apparatus to characterize fat release of food.

TABLE II

Correlation between Fat Release from Foodstuffs and Specific Antioxidant Migration from LD-PE after 5 Days

				Quantitative determination	
Foodstuff	Dry matter (%)	Fat content (%)	Fat i.d.m. (%)	Fat in PE (μg)	Antioxidant in foodstuff (μg)
HB 307	100.0	100.0	100.0	3840	138.8
Gouda cheese	55.0	27.2	49.5	3420	156.0
Margarine	80.0	80.2	99.3	2320	128.3
Creamed quark	24.4	10.2	41.8	1870	51.3
Creamed quark	22.2	6.1	27.5	1860	46.7
Olive oil	100.0	100.0	100.0	1760	134.0
Chocolate	100.0	30.5	30.5	1220	55.8
Mayonnaise	90.0	80.0	89.0	960	39.7
Soya bean meal	89.0	23.1	26.0	870	57.7
Processed cheese	51.9	26.0	50.1	325	2.0
Coffee cream	17.9	10.0	55.9	255	3.5
Skim milk quark	18.4	n.d.	–	60	0.4
Defatted soya bean meal	96.9	0.9	0.9	40	<0.1
Yoghurt	12.8	3.7	28.9	20	1.6
Water	0	0	0	20	0.4

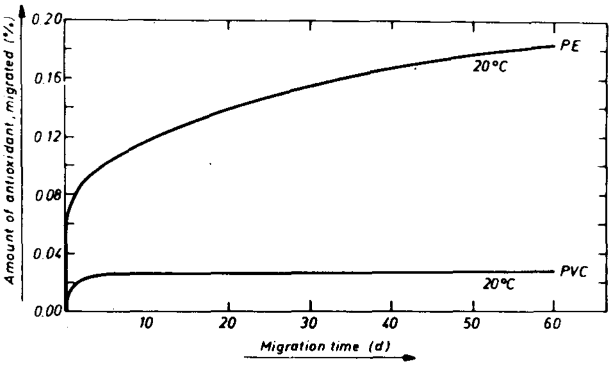

FIG. 3. Migration of antioxidant into sunflower oil.

to increase the diffusion coefficient to such a degree that measurable migration occurs (Fig. 3).

The migration of another antioxidant out of PP (2) into aqueous acetic acid is just measurable (Fig. 4). Again, there is no interaction between the test food and the packaging material PP. If the triglyceride HB 307 is used as test food, an interaction is found and an enormous increase in migration, too. (Test fat HB 307 (2,3), developed by us, is a standardized synthetic mixture of triglycerides which is stable, nearly free of impurities and has a melting point of about 28 C.)

The interaction of PE containing BHT as antioxidant and tricaprylin (TC) as test food—which as a homogeneous triglyceride gives clearer results—has been investigated by Figge (4) in more detail. After certain periods of contact, the polymer samples were separated from the tricaprylin, deep frozen and then cut into thin slices, for which the concentration of residual BHT as well as the intruded tricaprylin were quantitatively determined. The profile of the BHT concentration in the polymer block which has been in contact with TC on both sides is described as solid curves with the contact time t as parameter (Fig. 5). The broken curves represent the concentration of tricaprylin in the PE slices. It takes 850 hr at 40 C for a measurable amount of TC to reach the center of the PE-block with a thickness of ca. 1400 μm. The PE sample did not increase in thickness, although up to 15 mg triglyceride/g PE had been taken up.

In the system HI-PS containing 0.25% BHT as migrant in contact with tricaprylin as test food, again there was a decrease in concentration of the BHT, but a different distribution of the fat in the PS sample (Fig. 6). In this

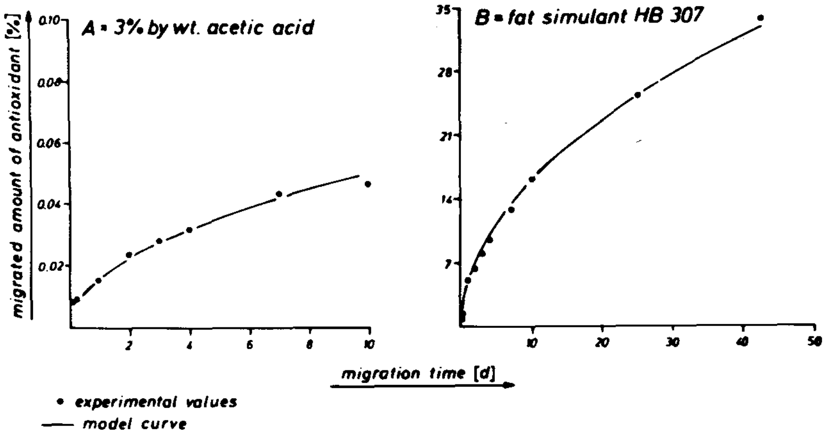

FIG. 4. Time dependence of the migration of antioxidant from polypropylene into A and B.

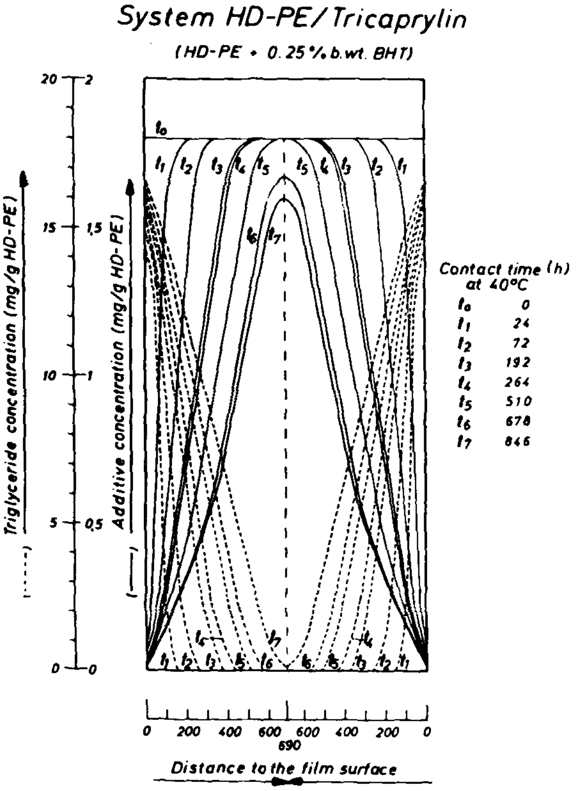

FIG. 5. Distribution of concentration for tricaprylin in HD-PE-test samples after different contact times (t_0 - t_7).

case, the boundaries between swollen and unswollen PS are quite distinct and the increase in thickness of 1,900 µm at the beginning and of 2,300 µm after 670 hr at 40 C. The uptake of fat of the outer layers reached 1,000 mg of triglyceride/g of PS. This large volume increase of the PS is the reason for its tendency to stress-crack.

Although the behavior of BHT is by no means typical for plastic additives as shown by numerous experiments, comparing other antioxidants and lubricants to BHT, BHT was used for this study due to the simplicity of radioactive labeling of BHT.

Rudolph (5) has developed a formulation of Fick's theory describing the behavior of plastics in contact with food. For this purpose a model has been used. In this model, we have three phases (Fig. 7): the polymer, the mixing phase of polymer/test food which might be swollen, and the test food or foods. The diffusion is to be considered only in one dimension, perpendicular to the interphase polymer/test food or food. The diffusion coefficient in the polymer and in the test food is considered to be constant, whereas in the mixing layer the diffusion coefficient is dependent on time and distance from the surface. The temperature is considered to be constant. The diffusion of the food component and the polymer additive must follow Fick's law, i.e., follows $\sqrt{t}$ kinetic. Discontinuities of concentrations of additives and fat at the phase boundaries are permitted.

The behavior of solid or highly viscous fatty food differs from that of liquid fatty food. In the liquid food, an even distribution of the migrated additive in each liquid phase is assumed. In highly viscous, homogeneous food, there will be a concentration gradient, with the highest concentration of additive at the contact layer to the packaging material. In both cases a certain migration of food components into plastic may occur. Food components always have a gradient of concentration within the plastic.

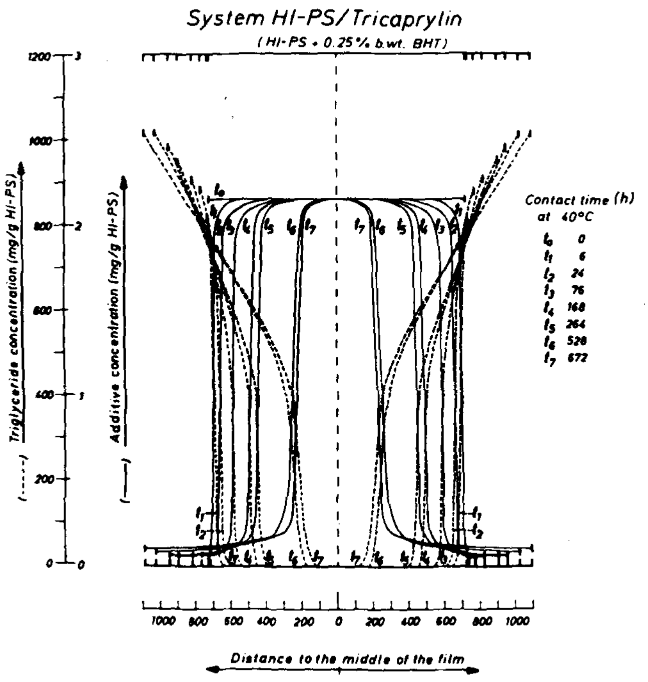

FIG. 6. Distribution of concentration for tricaprylin in HI-PS-test samples after different contact times (t_0 - t_7).

The solution of the model equations previously derived (5,6) gives, for the amount of additive migrated, $M(t) = \alpha C_A^P \sqrt{t}$. The amount migrated at the time t is proportional to the concentration C_A^P of additive A in the polymer P, and the square root of time. α is a complex function of the diffusion coefficients of the additive in the different phases and the Nernst partition coefficient of the additive between the polymer and the test food F, but not of time:

$$\alpha = f[D_A^F, D_A^P; k_1, k_2; \eta_x, \int_0^{\eta_x} \frac{\exp\{-F(u^2)\}}{D_A^{F+P}(u)}\, du, F(\eta_x^2)]$$

$$\eta_x = g(k, C_F^P, C_F^F)$$

$$F(\eta_x^2) = \int_0^{\eta_x} \frac{du^2}{D_A^{F+P}(u)},$$

where k_1, k_2 = partition coefficient for A; k = partition coefficient for F; and C_i^k = initial concentration of i in k.

If a food component is diffusing into the mixing phase in the case of interaction, the diffusion coefficient D_A^P is dependent on concentration of the food component in this polymer layer; in any case, the diffusion coefficients depend on temperature.

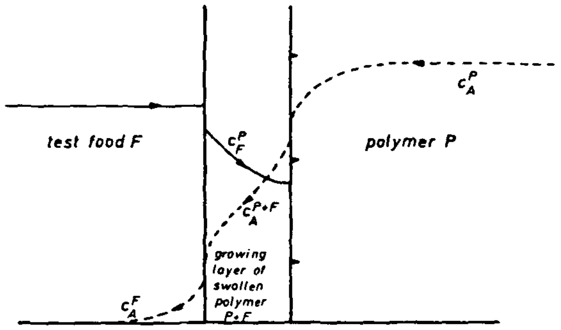

FIG. 7. Model of the system polymer/test food.

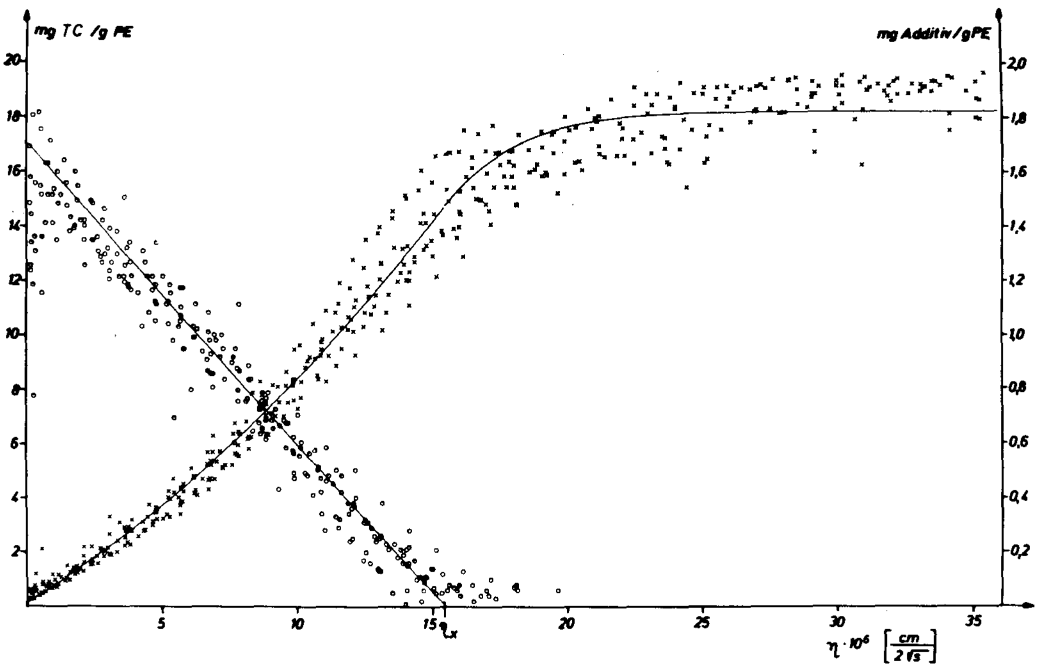

FIG. 8. Comparison of the measured values with theoretical curves for HD-PE: curve o = concentration of tricaprylin in the polymer as function of $\eta = x^{-}/2\sqrt{t}$; curve x = concentration of the additive in the polymer as function of $\eta = x^{-}/2\sqrt{t}$; x^{-} = distance from the boundary layer.

Using this theoretical formulation, we are able to describe quite precisely the behavior of additives in polyolefins (Fig. 4) and in PVC. Moreover, we can transfer the results given in Figure 5, i.e., the migration of BHT from HD-PE into the test fat at different times into two curves only if we use as abscissa the quotient $\eta = x/2\sqrt{t}$ with x being the distance of the investigated slices from the interface food/polymer (Fig. 8). The theoretical curves very well represent the measured data compiled in the previous figure. This result proves the validity of our assumptions. For now, we have solved the problem with systems of strong volume increase as we did with PS in contact with tricaprylin (7).

Investigations of Kashtock et al. and Gilbert (8-10) with vinylchloride have proven that there is a definite binding to PVC in the sub-ppm-concentration range. Recent investigations by Karcher and Schwarz/Petten (personal communication) in cooperation with Figge have revealed that polar additives—even at the percent addition level—show rather stable complexes with a polyamide. In such cases, the concentration in our initial equations has to be the concentration of the free, and therefore, diffusable molecule, which can be calculated according to Koros and Hopfenberg (11) considering a Langmuir or Freundlich binding characteristic. Then the equations have to be solved again. The results of this equation can no longer be described in closed form.

FINAL REMARKS

Because of the results of these investigations, we think that in directives dealing with plastics for food packaging it is possible and advisable to control the composition of the packaging material, as there is a definite mathematical relationship between the concentration in the material and the transfer into test food or actual food. With such a system, the control of the material will become unequivocal, and nevertheless, simple and very effective. We think it necessary that a law be reasonable, i.e., it should not be contradictory to the laws of the natural science and at the same time should be as simple and understandable as possible. Therefore, we prefer legislation regulating the packaging material composition to a legislation based on migration limits which are difficult to determine, and, therefore, difficult to guarantee or control.

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