

Diffusion of Phthalic Acid Esters from PVC Milk Tubing

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At the beginning of our work on diffusion processes in PVC tubing used in milk collection it was observed that plastic tubes which have been used for extended periods lose their originally smooth inner surface (1). In spite of careful maintenance, fine tears arise, forming a network on the inside which is in contact with milk, water, and cleaning solution (Fig. 1).



FIGURE 1. Small tears on the inside of PVC tubing after use in milking for about 1 year (1).

Moreover the special recommendation (2) of the Bundesgesundheitsamt, Federal Bureau of Health) of 1967, referring to the composition of PVC tubing used in milking, gave further impetus for studies on the behavior of such tubes in contact with milk as well as cleaning and sanitizing solutions. The cited recommendation prescribes that PVC

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milk tubes be plasticized mainly by a polymeric plasticizer based on adipic acid. Only 20% of the total plasticizer content is allowed to be monomeric. Phthalic acid esters (PAEs) are permitted as such monomeric plasticizers. In connection with this recommendation on the composition of such tubing, we were very interested in the extent to which the use of a polyadipate plasticizer is able to diminish the diffusion of monomeric plasticizers like phthalates out of the tubing.

Test Tubing and Principles of Testing Methods

Composition of the Tubing

The composition of the tubing used in most of the tests is shown in Table 1. Only for a few experiments have we used tubing of somewhat different composition; this is given in connection with the special results.

Table 1. Chemical composition of the test tubing

Constituents	Content of components, %		
	Tubing 1	Tubing 3	Tubing 4
PVC	52.3	67.0	47.5
Polyadipate	—	26.8	47.5
Dinonyl phthalate	47.2	—	—
Di-2-ethylhexyl phthalate	—	5.5	—
Stearic acid	0.1	0.2	0.2
Ca and Zn salts of fatty acids	0.4	0.5	—
Aminocrotonic acid ester	—	—	4.8

Special Equipment for Contact of Milk Tubing with Fluid Media

For the purpose of simulating practical use of tubing in milk collection under standardized conditions Kiermeier et al. (3) have developed a simple simulator (Fig. 2). It consists of three separate containers for water (B), milk (A), and cleaning solution (C), respectively. The two latter ones may be heated by thermostatic regulation. Each fluid is propelled through the equipment by a special pump. Electromagnetic valves control supply and drain of the fluids. Thus milk, water, and cleaning solution alternately flow through the test tubing, which connect two metal funnels, each of which has eight nozzles. Therefore eight tube sections can be tested together. For the flow back of milk and cleaning solution, respectively, additional sections of tubes can be provided. Each set of tubes is exclusively in contact with milk or cleaning solution. This permits testing of the influence of these fluids upon the tube materials.

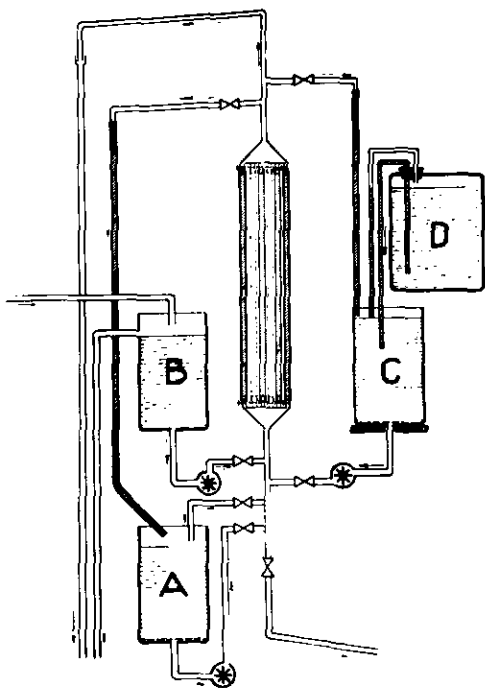


FIGURE 2. Flow-through equipment for milk tubing.

By means of this simple apparatus it was possible to simulate the conditions of practical use in a well controlled manner. The following periods for pumping the fluids through the tubes were chosen: Milk, 15.0 min; water, 3.5 min; cleaning solution, 8.0 min; water, 3.5 min.

Cleaning solutions A, B, and C are solutions of various detergents normally used for cleaning and sanitizing milking plants.

Thus the one milking cycle was reduced to 1/2 hr; it should be mentioned, however, that no time was allotted for drying between the different cycles. After a fixed number of flow-through cycles the tubing was tested for fat which had diffused in ("immigrated") or for further evidence of diffusion of plasticizer out of the tubing ("emigration").

In order to get small volumes of fluids for isolating emigrating PAEs we used rotating equipment (Fig. 3). The tubing, new or treated in the flow-through equipment, was rotated at a rate of 1 turn/min through a thermostatically controlled water bath. For this purpose we filled the tubing with the test solution and formed a ring by use of a small Teflon connector.



FIGURE 3. Equipment for rotating tubing filled with milk or cleaning solution.

Principle of Photometric Determination of Emigrated PAEs

Determination in milk—The sample was hydrolyzed by heating with hydrochloric acid. Milk fat and phthalates were quantitatively extracted by petroleum ether. The extract was dissolved in methanol, the bulk of milk fat was separated by freezing, the phthalates and the remaining fat residues were saponified with lye, and the free fatty acids were precipitated. Finally the phthalate in ethanol was determined spectrophotometrically at 284 nm.

Determination in cleaning solutions—PAEs migrating into cleaning solutions were extracted from the acidified samples with petroleum ether. The dried extract was dissolved in ethanol and the phthalates quantitatively determined as described above.

Diffusion Into Milk Tubing

Migration of Water

As expected, the diffusion of water into the tubing initially follows Fick's law, i.e., it increases linearly with the square root of time. In later stages the rate of diffusion tapers off, the water content within the plastic material reaching a limit. The rate of water diffusion evidently depends on the kind of plasticizer used: PVC plasticized by dinonyl phthalate shows the slowest rate of immigration of water; on the contrary, poly-

adipate increases the rate of water absorption. Thus PVC only containing polyadipate absorbs the highest amount of water within the period investigated (Fig. 4).

The results summarized in Table 2 clearly demonstrate that the diffusion of water into PVC tubing does not depend on the composition of the contacting solution. In addi-

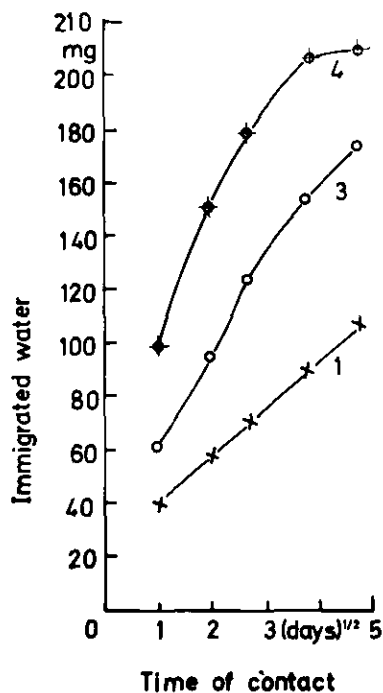


FIGURE 4. Migration of water into PVC tubing stored in distilled water (40°C) as a function of time. Tubing sections, about 5 cm; water absorption calculated for 10-cm sections.

Table 2 . Immigration of moisture from test fluids into PVC tubing. ^a

Type	Test fluid		Moisture migrated into tubing, % ^b		
	Concentration, g/l.	Surface tension dyne/cm	5	6	7
H ₂ O (distilled)	—	72.8	1.30	2.00	5.43
Na laurylsulfonate	0.35	45.7	1.33	2.03	5.43
NaOH	2.00	72.8	1.40	2.09	5.10
NaOH + Na lauryl-sulfonate	2.0 + 10.0	33.3	1.33	2.16	4.95

^a Contact, 14 days at 20°C.

^b Tubing: A = PVC-dinonyl phthalate (65/35); B = PVC-dibutyl phthalate (70/30); C = PVC-polyadipate ester (59/41).

tion the results with tubing⁷ again confirm the strongly promoting effect of polyadipate on the water immigration into plasticized PVC.

Migration of Milk Fat

Tests on the diffusion of fat into plasticized PVC lead to completely different patterns than tests on water diffusion. While polyadipate enhances the immigration of water into plastic, it retards the absorption of fat by plastic continuously in contact with milk. PVC plasticized with PAEs absorbs larger amounts of milk fat the higher the phthalate content (Fig. 5).

Milk represents an oil-in-water emulsion. Therefore it seems reasonable for both phases to invade the plastic. The overlapping diffusion of water seems to increase the rate of fat absorption. This fact explains why the diffusion of fat from milk does not fulfill Fick's law; the absorption of fat is, rather, a linear function of contact time (Fig. 5).

The assumption that immigrated water accelerates the fat absorption is supported by the observation that less fat migrates into PVC tubing containing phthalate if the tube is continuously in contact with milk than if the tubing is alternately in contact with milk, water, and cleaning solution (Table 3).

At first sight this fact is very surprising. To explain it, one must consider that during contact with milk a fat layer is spreading over the PVC surface. The layer is built up of "free" milk fat. This fat layer gradually inhibits the migration of water into the plas-

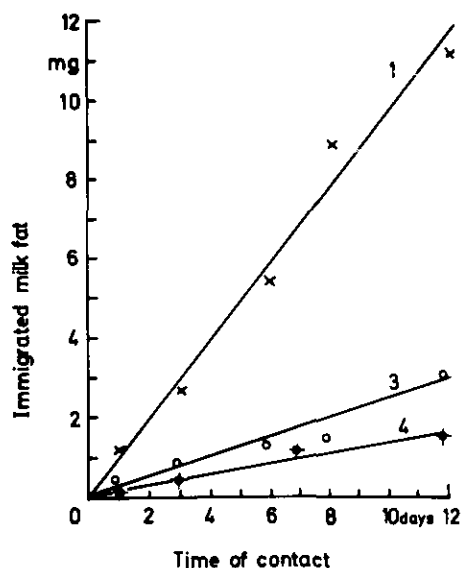


FIGURE 5. Migration of fat from raw milk (38°C, about 4% fat content) into plasticized PVC as a function of time of contact.

tic material. If this fat layer is periodically removed, the water phase is capable of invading the tubing relatively rapidly, especially during cleaning at 40°C. This soaking of the plasticized PVC apparently favors the subsequent diffusion of fat into the material. It still remains to be examined to what extent warming of the PVC by the heated solution additionally increases the rate of fat absorption.

Diffusion of PAE Plasticizers from PVC Tubing into Contacting Fluids

In considering the migration of PAEs from plasticized PVC in fluid media it is

Table 3 . Absorption of fat into PVC tubing in contact with milk only and tubing alternately in contact with milk at 20°C, water at 14°C, and cleaning solution at 40°C. ^a

Contacting fluids	Time of contact with milk,		Immigrated fat, mg
	hr.		
Milk	120		24
	336		124
Milk, water, and cleaning solution alternating ^b)	45		80
	90		123

^a A 1-m length of tubing was used.

^b Rates of contact: 15 min milk, 15 min water, and cleaning solution alternating between both.

necessary to distinguish between new samples which have not been soaked by water and tubing in a soaked state.

Migration of PAEs from New Tubing

Migration into cleaning solutions—In order to control the release of PAEs into cleaning solutions, we filled the tubing with 100 ml of the solution and rotated it for 24 hr at 40°C in the apparatus described above. Subsequent analysis of the solution showed that partial substitution of a polyester of adipic acid for phthalate definitely decreases the absolute amount of phthalate emigrating. Differences between the cleaning solutions with regard to extracting effectiveness are very small (Table 4). During analysis, on acidifying the solutions, marked flocculates were observed. They could be identified as long-chain fatty acids. The emigration of these substances can be explained by the assumption, that the originally insoluble Ca and Zn salts of fatty acids as well as stearic acid in the PVC react with the alkali ions. They thus become well capable of migrating into the cleaning solution. Furthermore the reaction products may favor the emigration of phthalate plasticizers (4). This fact may be defined as an "inverted carrier effect."

Table 4 . Emigration of phthalic acid esters from PVC tubing into cleaning solution. ^a

Cleaning solutions	Phthalate migration from tubing, mg/100 ml	
	Tubing 1	Tubing 3
A	2.2	0.5
B	2.8	0.5
C	2.3	0.5

^a Length of tubing, 1m; volume of cleaning solution, 100 ml; time of contact, 24 hr; 40°C. Cleaning solutions A, B, and C are solutions of various detergents normally used for cleaning and sanitizing of milking plants.

Finally, the alkali may hydrolyze the PAEs themselves. The resulting alkali salts of phthalic acid should possess an increased tendency for migration out of the PVC.

Migration into Milk—Milk is a more effective extracting agent than any of the examined cleaning solutions. Table 5 demon-

strates, moreover, that tubing 3, plasticized by a mixture of polyadipate and phthalate, loses a smaller absolute quantity of the phthalate than tubing 1, which contains monomeric PAE only. Relative to the phthalate content, however, the tubing with polyadipate releases a higher amount of phthalate than the tubing plasticized by dinonyl phthalate only (Table 5). Moreover, Table 5 demonstrates the expected accelerating effect of temperature on the diffusion of PAEs from PVC tubing (5).

Table 5 . Migration of phthalic acid esters from PVC tubing into milk (100 ml; time of contact: 24 hours) and into cleaning solution A. ^a

Tubing type	Phthalate migration, mg/100 ml		
	Into milk at 38°C	Into milk at 56°C	Into cleaning solution at 38°C
1	4.6	7.0	2.2
3	2.0	3.1	1.1

^a Length of tubing, 1 m; volume of milk, 100 ml; contact time, 24 hr; volume of cleaning solution, 100 ml; contact time, 24 hr. Cleaning solutions A, B, and C are solutions of various detergents normally used for cleaning and sanitizing of milking plants.

Migration from Used (Soaked) Tubing

In practice, during milking and cleaning periods, moisture passes into the PVC tubing, which gradually grows dull. Therefore we tested the migration of PAEs from tubing without or after contact with water. As is evident from the results in Table 6, the absolute loss of PAEs depends on the phthalate content of the plastic material. In addition, the previous absorption of moisture by the plasticized PVC significantly increases the migration of PAEs from the tubing. This is especially true for tubing 1 (Table 6).

Like the storage of the tubing in water, the alternating flow of milk, water, and cleaning solution through the tubing also increases the emigration rate of PAEs. Compared with new tubing, old tubing which has been aged in the simulator for up to 180 hr shows an elevated tendency to release PAEs into milk. After 360 hr of alternating

Table 6. Migration of PAEs into milk from PVC tubing with and without absorbed water.^a

Time of tubing contact with water, days	Phthalates migration from tubing, mg/100 ml	
	Tubing 1	Tubing 3
0	4.6	2.0
7	7.3	2.5
14	9.5	2.5

^a Volume of milk, 100 ml; time of contact, 8 hr; 38°C.

contact with the various fluids in the simulator, the loss of phthalates from the tubing apparently declines again (Fig. 6). This may be explained by the fact, that the PVC layers near the inner surface have become poor in phthalates, which are unable to diffuse sufficiently rapidly from the interior of the tubing.

Theories of the Diffusion Behavior of PAE Plasticizers in PVC Milk Tubing

A comparison of the absolute quantities of emigrating PAEs clearly demonstrates that it is possible to reduce the release of PAEs from PVC tubing significantly by replacing them for the most part by polyadipate plasticizer. To evaluate the influence of the polyadipate on the emigration of PAEs from plasticized PVC, one must remember, however, that the ratio of phthalates in tubing 3 and 1 nearly corresponds to 1:8.5, but without presoaking, the ratio of the amounts of phthalates released into milk is only 1:2. From this one may conclude that polyadipate in tubing 3 occupies or screens most of the adhering points of the PVC. Under

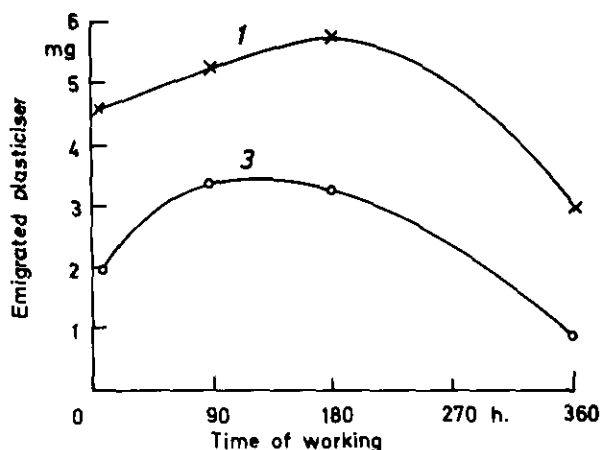


FIGURE 6. Migration of PAEs from PVC tubing (1 m) into milk as a function of duration of previous alternating contact with milk, water, and cleaning solution (time of contact: 8 hr at 38°C).

these conditions the monomeric phthalate is not completely solvated but is predominantly freely mobile. On the other hand, in tubing 1 about 40% of the total phthalate should be fixed in the PVC (6) and thus unable to migrate. The ratio of unsolvated phthalates able to migrate reasonably may be about 1:4.9 for tubing 3 relative to tubing 1. This value is approximately equal to the highest ratio of phthalates migrating from the two types of tubing (Table 7).

According to Thinius (7), the total quantity of all the more or less hydrophilic additives within the PVC determines the amount of water absorbed by the plastic material. Therefore, plasticizers play a major role, because they are the predominant additive used in PVC. The amount and chemical structure (8) of the plasticizers in the PVC determine how much water can

Table 7. Dependence of ratio of amounts of phthalates emigrating from PVC tubing into milk or cleaning solution A on presoaking of the tubing with water. ^a

Contacting fluid	Conditions of contact		Time of presoaking, days	Ratio of amounts of phthalates migrating (tubing 3:tubing 1)
	Temperature, °C	Time, hr		
Milk	20	8	0	1:2.0
	38	8	0	1:2.3
	56	8	0	1:2.3
	38	8	7	1:2.9
	38	8	14	1:3.8
Cleaning solution	40	24	0	1:4.4

^a See table 4 for explanation of cleaning solution A

immigrate. The water molecules pass through the PVC chains, which are relaxed by the plasticizers. Presumably, the immigrated water molecules adhere especially to unsolvated phthalate molecules, which are ultimately responsible for the plasticizing effect in PVC, when mechanically stressed. Thus it seems reasonable, that the absorbed water makes the tubing less flexible (9). Apparently the hydrated phthalate molecules are no longer able to solvate at points of increased tension if the tube is bent. Unlike the monomeric phthalates, polymeric plasticizers like polyadipates act primarily by the screening effect of their paraffin chain, while adhering to the PVC dipoles with the polar ester groups (10). Therefore this kind of plasticizer does not have to migrate to points of increased tension to be effective. This is the reason why PVC plasticized by polyadipate remains pliable in spite of increased water absorption (Table 8).

Parallel to the partial loss of flexibility, tubing having absorbed water always show an increased tendency to release phthalate. We think that the immigrated water covers the polar groups of the unsolvated phthalates and thus prevents the molecules from adhering to residual free PVC dipoles. Consequently, the hydrated phthalate molecules with screened ester groups are more mobile and less hindered in their way through the PVC network compared with material free from immigrated water. The latter thus operates like a vehicle which ac-

celerates the diffusion of PAEs into contacting fluids.

After soaking for a period of 14 days the phthalates tend to migrate faster out of the tubing 1 (without polymeric plasticizer) into milk. From the unsoaked tubing only about twice the quantity of phthalate migrates than from tubing 3 with polyadipate. Because of hydration of the PAEs, this ratio is increased to roughly 1:4. This value is nearly the same as the ratio of freely mobile phthalates in the two materials. In contact with the cleaning solution and without preceding absorption of water, a similar ratio is observed.

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Table 8. Force required to crush the profile of PVC tubing with and without immigrated water.

Tubing type ^b	Force to crush tubing, kp/m ^a		Difference in pressure, %
	Unsoaked	Soaked	
3	5.4	6.8	26
4	7.2	7.2	0

^a Crushing distance, 5 mm; tubing inside diameter, 12 mm; tubing wall thickness, 3 m; presoaking with water, 18 days at 40° C.

^b Unfortunately tubing 1, containing only phthalate plasticizer, was too flexible and thus could not be measured by the method used.