

Plasticized Poly(Vinyl Chloride) / Dioctyl Phthalate / Petroleum Oils: Plasticizer Migration vs. Liquid Penetration

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Synopsis

Previously presented migration data on the systems poly(vinyl chloride) (PVC)/labeled dioctyl phthalate (DOP)/white spirit, kerosene, white oil, or lubricating oil are now combined with liquid penetration results. Liquid penetration was found to be significant for the lighter oils while the white oil and the lubricating oil practically seem not to penetrate at all. In accordance with previous investigators this penetration phenomenon was proved to consist of a sorption step up to a point, followed by a desorption step. Both steps were considered separately but the desorption data failed to fit the short-term Fickian approximation. On the other hand, in order to explain the minimum observed, as temperature increases, of the migration equilibrium values, it is proposed a polymer structure rearrangement to a more compact scheme at the later stages of the immersion experiments. For this rearrangement both temperature and liquid penetration seem to comprise contributing factors.

INTRODUCTION

In most plastics-producing countries PVC is among the leading plastic materials. The greater part of PVC is used as plasticized PVC and PVC applications consume a high percentage of the total production of plasticizers.

In all applications plasticized PVC is in contact with some kind of surrounding medium. The plasticizer may stay in place, or (more usually) it may migrate to the surrounding medium. In the latter case, the polymer itself shows considerable change in mechanical properties while the surrounding medium is contaminated. The problem becomes extremely serious in the case of packaging with plasticized PVC films foodstuffs and pharmaceuticals.

It is well documented that in the usual case of plasticizer migration in solid/liquid systems the phenomenon is very often accompanied by liquid penetration into the plastic.¹⁻⁸ Such an interaction may result in an ever-thickening inhomogeneous layer of mixed polymer and liquid medium, and then the problem belongs to the general class of diffusion processes with moving boundaries.^{9,10} On the other hand, it has been definitely confirmed that the plasticizer-liquid medium mixture may become gradually a nonsolvent and then separate as a second phase in the mass.^{5,6} Accordingly, a great amount of research work has been also oriented toward establishing and solving the corresponding implications of the diffusion mathematics. However, the general applicability of some of the models proposed still remains limited.

In a previous work from our laboratory¹¹ long-term migration data were presented for the systems PVC/dioctyl phthalate (DOP)/petroleum oils, namely white spirit, kerosene, white oil, and lubricating oil. In particular, the migration behavior was followed until equilibrium at three temperature levels and Fickian behavior with constant diffusion coefficient was confirmed for the initial stages of the process. However, as discussed in this article, liquid penetration was found to be very high for the lighter oils while the viscous white oil and lubricating oil seem not to penetrate at all. Accordingly these counterdiffusion processes were carefully monitored, simultaneously with the migration process. A qualitative model for explaining the overall behavior in terms of polymer structure alteration has been also included.

EXPERIMENTAL

Reagents

As previously described.¹¹

Synthesis of Labeled Dioctyl Phthalate

As previously described.¹¹

Plasticization

As previously described.¹¹

Immersion

Each of the specimens was immersed in 250 mL liquid contained in a glass-stoppered Erlenmeyer flask of 300 mL. All tests were made in duplicate and the flasks were kept in an oven fixed at three different temperature levels: 37, 50, and 70°C ($\pm 1^\circ\text{C}$). To monitor weight changes, the specimens were removed from the liquid environment, wiped gently with a tissue, and immediately weighed.

Radioactivity Measurements

As previously described.¹¹

RESULTS AND DISCUSSION

As already referred to,¹¹ the total amount of plasticizer migrated at immersion time t is represented by Q'_t and it is determined by measuring the radioactivity of the liquid medium. The amount of the latter, counterdiffused into the plastic film at the same time t , is represented by S'_t and it can be calculated by the following equation⁸:

$$S'_t = (W_t - W_0) + Q'_t \quad (1)$$

where W_t and W_0 represent the weight of the specimen at time t and zero, respectively. In Figures 1, 2, and 3, corresponding to the three temperature levels tested, curves of Q'_t/l vs. t and S'_t/l vs. t are given for both white

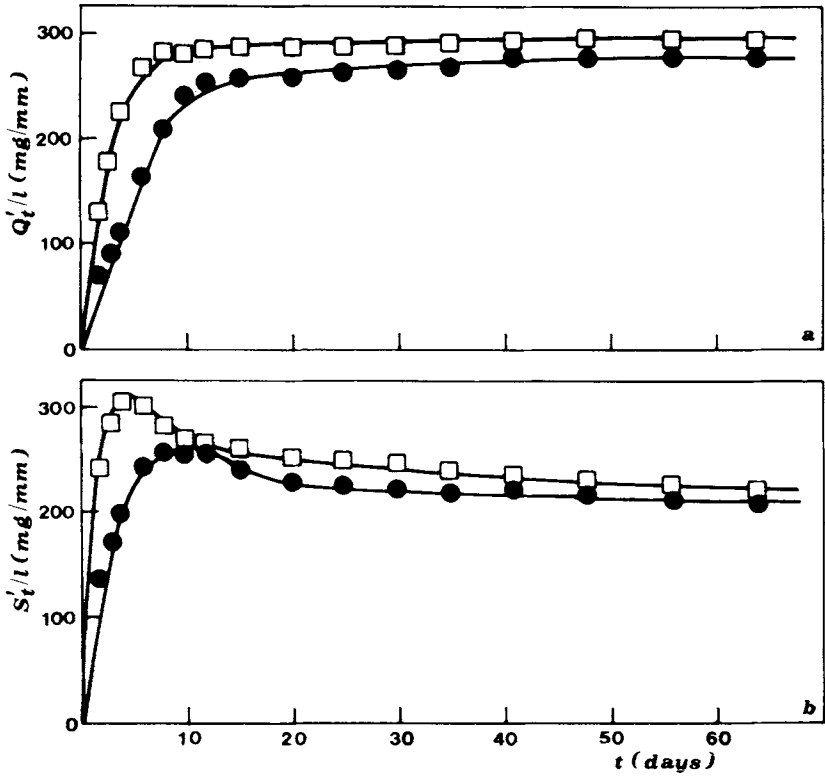


Fig. 1. Plots of plasticizer loss (a) and penetrant uptake (b) vs. immersion time at 37°C: (●) kerosene; (□) white spirit.

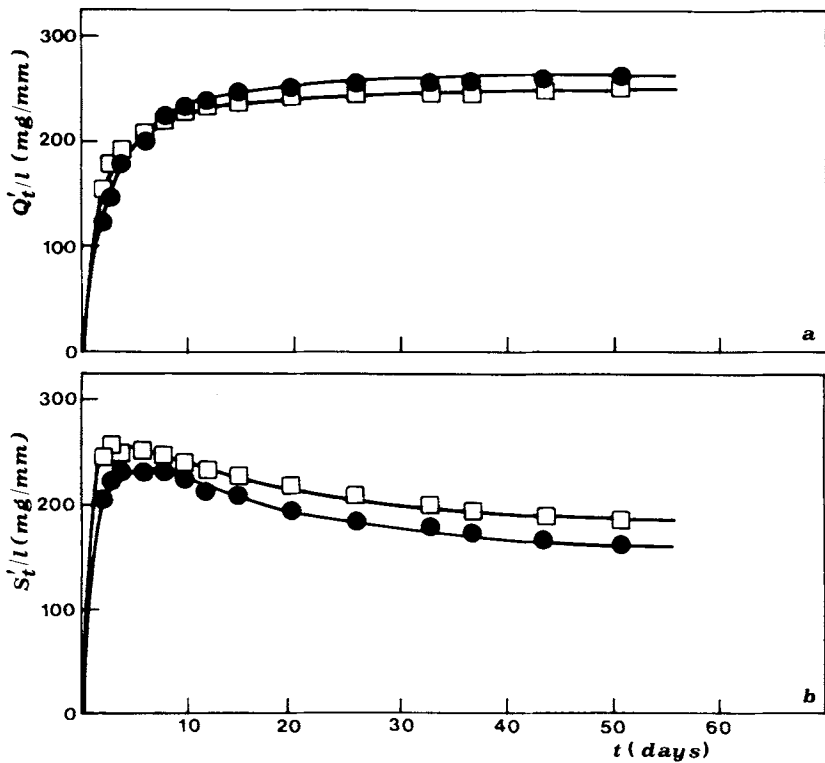


Fig. 2. Plots of plasticizer loss (a) and penetrant uptake (b) vs. immersion time at 50°C: (●) kerosene; (□) white spirit.

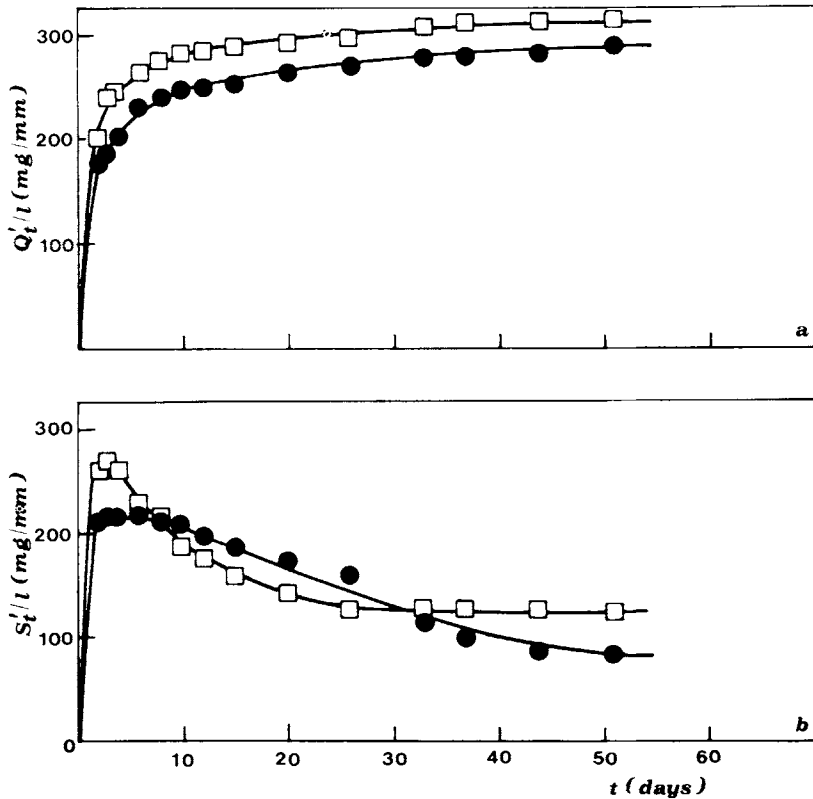


Fig. 3. Plots of plasticizer loss (a) and penetrant uptake (b) vs. immersion time at 70°C: (●) kerosene; (□) white spirit.

spirit and kerosene. In accordance with previous studies,^{5,6,12} Q'_t and S'_t have been reduced per mm of the specimen thickness so that slightly different specimens can be readily compared. No curves are presented for white oil and lubricating oil since the corresponding penetration levels continuously fall near zero.

Confirming similar data by Messadi and Vergnaud^{13,14} studying the system PVC/DOP/benzyl alcohol or ethanol-water, all curves of S'_t/l vs. t pass through a maximum. In other words, the amount of white spirit or kerosene transferred into PVC increased at the beginning of the immersion, rose to a maximum value, and then decreased. Thus, the counterdiffusion process comprises a two-step phenomenon with a liquid transfer into and out of the PVC specimen.

Based on the data quoted in Figures 1, 2, and 3, in Table I are tabulated equilibrium values of the liquid counterdiffused, expressed on initial weight basis^{5,6} and also the maximum values attained, similarly reduced.

Both from the equilibrium or maximum values points of view it is clear that, in contrast with the white oil and the lubricating oil, considerable amounts of the lighter oils penetrate into the plastic film. As temperature increases, penetration either at equilibrium or at maximum is restricted to continuously lower values. On the other hand, it becomes clear [see also Figs.

TABLE I
Equilibrium and Maximum Values of Liquid Counterdiffused
(Expressed on Initial Weight Percentage Basis)

Temperature	Liquid environment	Kerosene	White spirit	White oil	Lubricating oil
37°C	Equil.	17.4	17.8	0.8	0.2
	Max.	21.7	24.6	0.9	0.5
50°C	Equil.	13.3	16.1	3.39×10^{-2}	—
	Max.	18.9	22.2	0.5	—
70°C	Equil.	7.0	10.4	—	—
	Max.	18.4	21.9	0.5	—

1(b), 2(b), and 3(b)] that white spirit penetrates, in general, in greater extent into the polymer in comparison with kerosene. Similarly the amount of plasticizer migrated is generally greater when white spirit is employed as liquid medium [Figs. 1(a), 2(a), and 3(a)]. The latter observation confirms the well-known fact of a direct correlation between the penetration ability of a liquid medium into plastics and the migration of low-molecular plastics components into this liquid.⁸ In fact, on the other extreme, white oil and lubricating oil do not penetrate, and the migration is similarly quite limited.¹¹

Macroscopic Observations

Counterdiffusion phenomena resulted in opacity. In fact, the initially quasitransparent specimens, after short-term immersion, became opaque, especially those immersed in white spirit. Nevertheless, since the appearance of a maximum in the curve S'_t/l vs. t substantially coincides when high migration rates are obtained (Figs. 1, 2, and 3), no considerable swelling of the specimens did happen. Furthermore, in agreement with previous observations,^{5,6} separation of a second phase was observed within the plastic mass.

Elementary Kinetics of the Liquid Penetration Process

It is a well-known fact that diffusion of relatively small molecules through rubbery polymers can in general be predicted on the basis of Fick's law. In a previous paper,¹¹ the problem of possible deviations in the case of solid/liquid plasticizer migration was discussed in detail. Nevertheless, under some assumptions, taking also into account the absence of swelling, the short-times approximation of the one-dimensional Fick's diffusion equation can be a good basis for trying to fit our experimental data:

$$Q'_t/Q'_\infty = 2(Dt/\pi l^2)^{1/2} \quad (2)$$

where Q'_t represents the total amount of diffusant sorbed or desorbed at time t , Q'_∞ the corresponding quantity after infinite time, D the diffusion coefficient supposed independent of concentration and time, and $2l$ the thickness of the PVC sheet.

As already mentioned, the counterdiffusion process has been proved to be a two-step phenomenon, i.e., consisting of a sorption step up to a point, followed

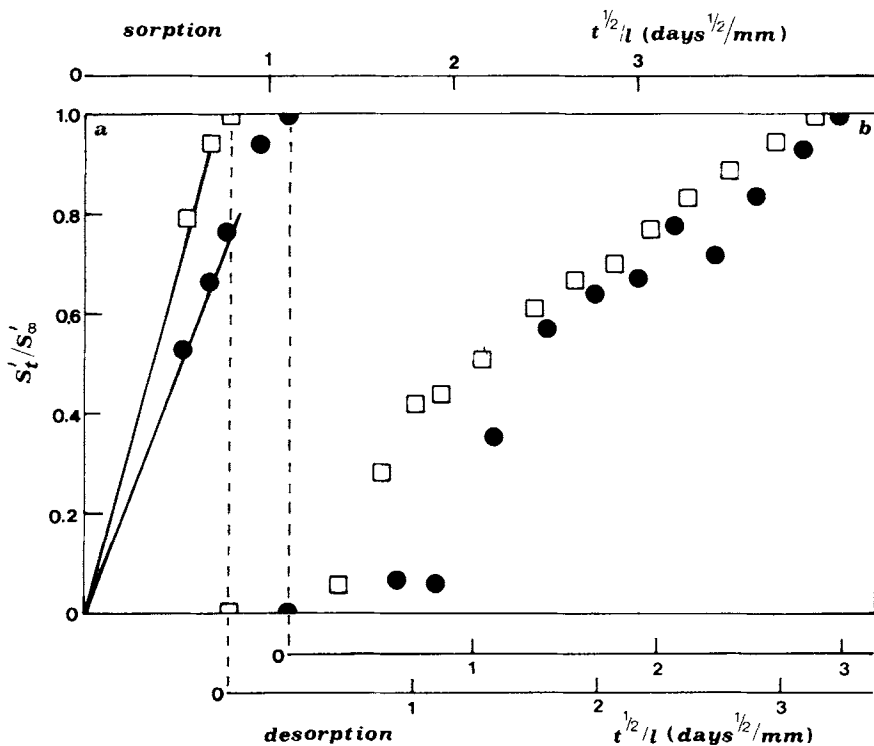


Fig. 4. Fickian (short term) correlation of counterdiffusion data at 37°C for the sorption (a) and desorption stages (b): (●) kerosene; (□) white spirit.

by a desorption step. Both steps were considered separately and the validity of eq. (2) was tested.

In Figure 4 corresponding to the temperature level of 37°C, the satisfactory conformity of the sorption data, at the initial stages, to eq. (2), can be seen for both white spirit and kerosene. It should be mentioned that the assumption was made according to which the maximum amount of liquid sorbed was considered as the equilibrium amount.^{13,14} On the other hand, for the desorption step, the same amount was supposed as initially contained in the sheet while the time of its appearance was defined as starting time ($t = 0$) of the desorption process.¹³

In Table II correlation coefficients for both steps (initial stages) can be seen accompanied by calculated diffusion coefficients for the sorption process where good fitting is confirmed. On the contrary, desorption data do not conform to eq. (2) and the same was valid at the higher temperature levels of 50 and 70°C, e.g., Figure 5 (50°C). On the other hand, for the sorption stage and at the higher temperatures tested, we found out that our data were not enough for a reliable test of conformity to the Fick's law (Fig. 5). This was due to the fact that the maximum value was attained quite earlier (see also Figs. 1, 2, and 3), and in future work more experimental points at the very initial stages should be collected. Therefore, diffusion coefficients for the sorption process at

TABLE II
Fickian (Short-Term) Correlation of Counterdiffusion Data at 37°C
Together with Corresponding Migration Data¹¹

Liquid environment	Sorption stage		Desorption stage		Migration D (cm ² /s)
	r^2	D (cm ² /s)	r^2	D (cm ² /s)	
White spirit	1.00	4.43×10^{-8}	0.64	—	1.83×10^{-8}
Kerosene	1.00	2.23×10^{-8}	0.79	—	7.07×10^{-9}

50 and 70°C cannot be evaluated with reliability; furthermore, no Arrhenius temperature dependence can be checked.

In spite of the above difficulties, comparison between the diffusion coefficients during the initial stages of both the plasticizer migration¹¹ and liquid sorption processes, at least at 37°C, is quite useful. Clearly, in both cases of white spirit and kerosene, sorption takes more readily place than migration. On the other hand, when white spirit is employed, the polymer, at least initially, seems more permeable to both plasticizer and liquid medium in accordance with previous discussion.

The consideration given up to now and concerning the coupled phenomenon migration/counterdiffusion refers to the initial stages of the process where

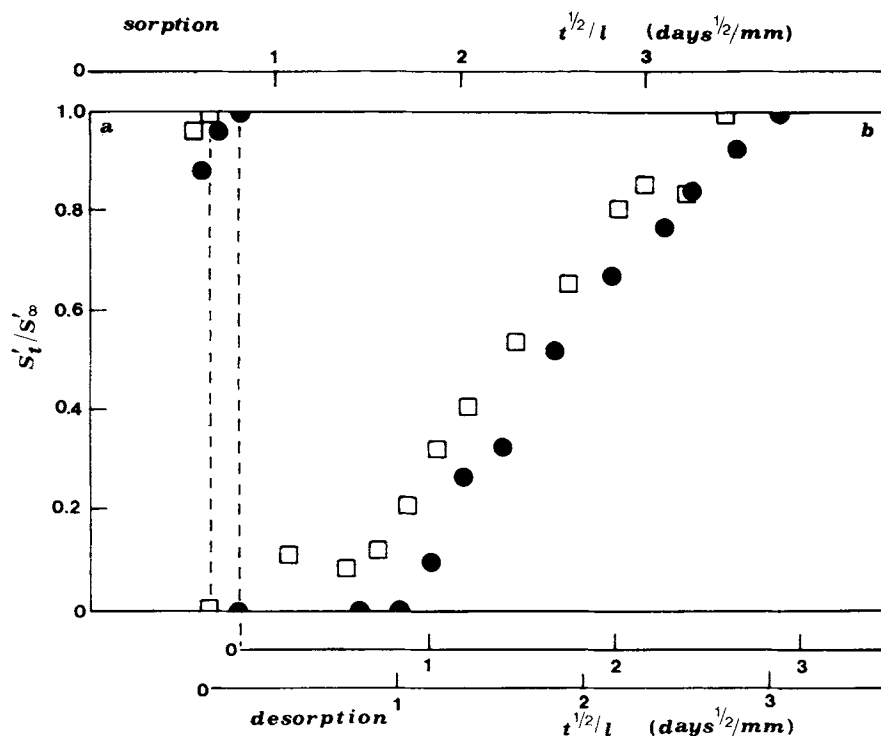


Fig. 5. Fickian (short term) correlation of counterdiffusion data at 50°C for the sorption (a) and desorption stages (b): (●) kerosene; (□) white spirit.

high rates both in migration and sorption are observed. Later, considerable transitions may happen to the polymer structure. Two points have to be emphasized:

(a) As plasticizer goes out, the system gradually turns to nonrubbery or nearly nonrubbery behavior, in agreement with macroscopic observations. This is particularly evident for the lighter oils in which high migration levels are exhibited. On the other hand, no considerable plasticization effect should be expected from the liquid medium penetrated, also due to its well-marked separation in a second phase. Accordingly, no conformity to long-term Fickian expressions with constant diffusion coefficient should be expected [e.g., eq. (4) in Ref. 11]. This has been confirmed also in our data in which the correlation coefficient did not exceed the level of 0.91. On the contrary, a very good conformity to the long-term expression is observed for the viscous, nonpenetrating white oil and lubricating oil (r^2 in the range between 0.98 and 1.00).

(b) A second point which may contribute more to the complexity of the overall phenomenon is concerned with the possibility of some rearrangement, during the immersion stage, of the polymer structure. In fact, commercial PVC comprises a semicrystalline polymer, although it has been proposed that a portion of the apparently crystalline material is in a mesomorphic condition with only two-dimensional order.¹⁵⁻¹⁷ In any case, during the immersion stage one cannot ignore the effect of the extremely extended maintenance of the material at the temperature level considered. In other words, a rearrangement of the structure to a more ordered and compact scheme may take place and this should also comprise another transition state possibly met during the overall process. Typical annealing experiments have been excessively carried out on rigid and plasticized PVC but the interest has mainly focused on the variations of the nodular structure observed.^{18,19}

We have collected experimental evidence of such a situation by carrying out particular experiments on this field,²⁰ but also in the present work, this hypothesis fits very well the equilibrium migration levels met for both liquids, white spirit, and kerosene. In fact, as emphasized already,¹¹ when immersion temperature increases from 37 to 50°C, the migration equilibrium values decrease and then start increasing again even if migration diffusion coefficients, at the initial stages, continuously increase. Subsequent rearrangement, at 50°C, to a better organized structure resisting plasticizer migration remains a good explanation; but, of course, when temperature increases to 70°C, the effect of the plasticizer loss is much more pronounced, while degradation effects cannot be ignored. Such a mechanism is also compatible with the broad maximum detected at 50°C of the curve S'_t/l vs. t especially for the more effective white spirit (Fig. 2). In other words, the more compact structure reduces also the desorption rate of the liquid counterdiffused. On the contrary, at 37 or 70°C these maxima are quite distinct (Figs. 1 and 3).

Besides temperature, the role of counterdiffusion fits also well the above-proposed "annealing" model. In fact, even if the noncompatible plasticizer-oil mixture does not result in evident plasticization of the material, due also to the sorption-desorption process, its presence may contribute to some mobility at molecular level favoring structure rearrangement. Furthermore, such annealing hypothesis could also be correlated with the considerable decrease of the maximum and equilibrium amounts of liquid sorbed when temperature

increases (Table I) for which, however, within our experimental limits, passing through minimum is not observed.

As a final comment it should also be mentioned that such a rearrangement/annealing model is also compatible with the fact that not all the plasticizer is removed even after 50–65 days immersion in the liquid media considered. In view of the infinite baths and negligible boundary effects assumption,¹¹ these experimental data, on the basis of such a model, might be explained.

CONCLUSIONS

Plasticizer migration in solid/liquid systems comprises an extremely complex process even if boundary surface phenomena and external resistance to migration are considered to be of minor effect. Furthermore, the liquid medium may counterdiffuse into the plastic. Loss of plasticizer results in transition of the material from rubbery to nonrubbery or quasirubbery state. Accordingly, conformity even to simple expressions of Fick's law is usually limited for the very initial stages of the process. On the other hand, the effect of migration temperature is very important and more complicated, due to possible annealing; i.e., it is suggested that the three-component structure (polymer–plasticizer–liquid) may rearrange itself to a more compact scheme.

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