ROOF COVERINGS MADE OF PVC SHEETINGS: THE EFFECT OF PLASTICIZERS ON LIFETIME AND SERVICE PERFORMANCE

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There are two types of plasticized PVC sheetings in common use. In the first type, the PVC sheeting is fixed on the foundation and its surface is directly exposed to the open air and weather. In the second type, the sheeting is covered with a layer of gravel to form a protective covering.

Because the stability of plasticizers in the PVC sheeting depends on the construction of the roof-covering, there are substantial differences in the life expectancy and service performance of these two types of PVC sheetings. The plasticizers are extremely important. A loss of plasticizer causes a change of mechanical properties. The material is hardened. The modulus increase in combination with the material shrinkage and rigidity causes considerable forces to occur, which very often result in damage within the material itself or between the material and the attachment points.

The description of plasticizers by the use of trade names is not sufficient. Worldwide about 500 plasticizers are offered, but very often only the trade names are different, not the chemical structure; about 70 percent of the used plasticizers are phthalic esters.

Identifying these plasticizers can be done by liquid chromatography. The plasticizer is extracted from the sheeting and the quantitative and qualitative analysis is rather simple. The plasticizer's content in a new sheeting is about 36 percent. A loss of 10 percent to 12 percent from that may damage or cause total destruction of the roof-covering. This damage and its repair are very expensive for the owner of the building and for the national economy. Therefore, it is interesting and important to study the loss of plasticizer and the correlation to its chemical structure.

At first we studied some roof coverings which failed during lifetime; the majority of the specimens were obtained from roofs covered with gravel. In some cases new material was restored, so we were able to compare the new material with damaged specimens.

Two results are very important:

1. The plasticizers very often are mixtures of different esters of phthalic acid.
2. The sheetings are mostly very thin, only with 0.8mm thickness.

In Germany it often is said that a thin sheeting is easier to handle, and the lower price is economically competitive.

All specimens we tested led to the same result: In a mixture of plasticizers those with the smallest molecule, i.e. phthalic-esters with alcohols with short chains, escape first off the sheeting.

The loss of plasticizers may arise by evaporation, migration, washout, hydrolysis, or by the life histories of microorganisms. The loss of plasticizers is independent from the aging, i.e., the degradation of macromolecules, but very often parallel to that. We studied the loss of plasticizers in correlation to their chemical structure under laboratory conditions and also by practical experience. We used commercial sheetings as well as those prepared with definite plasticizers for our experiments, with the kind support of industry. Figure 2 shows that the plasticizers with short chains evaporate more easily from the film than those with long chains. The loss of plasticizer containing C − 4 = buten structures is much higher than from the specimen with larger molecules. The measurements were made at 75C.

The evaporation of plasticizers may be important in southern countries but not in Northern Europe. The migration of plasticizers is more important. Plasticizers' migration into other substances, e.g. polystyrene, is well known. We studied the migration in this way by covering one side of the film with a plate of polystyrene, and the other we left open to the surrounding air, fixed only by a wire net. This specimen was stored about 600 hours at 75C. Figure 3 demonstrates in the same way the influence of short chains.

The migration is faster. Larger molecules are relatively retained. The temperature of 75C is comparatively high but a migration also takes place at lower temperatures; figure 4 shows the migration of plasticizers off commercial sheetings. Even a material used for seven years in practice, "A 18," still loses plasticizer.

Figure 5 shows the influence of the plasticizer's structure and the thickness of the sheeting on the loss of plasticizer. It is very clear that a plasticizer with branched long chains (i-8 and i-10) is much more stable against migration than one with short linear chains. A thicker sheeting loses less plasticizer than a thin one.

In conclusion, a sheeting with a thickness of 1.5mm and made with plasticizer with branched long chains has the best service performance. In this experiment some other problems of fabrication are not included.

Our laboratory experiments are confirmed by experience in practice. On the same roof, sheetings with 0.8mm and 1.5mm thickness were installed side by side and covered with a layer of gravel. During 10 years, the change of material properties was tested. Figure 6 demonstrates the loss of plasticizers and the corresponding increase of the modulus. It is very clear that the thick sheeting is only slightly deteriorated, but the thin sheeting is much more deteriorated and nearly useless.[1]

Figure 7 demonstrates the influence of the structure of plasticizers on the lifetime of a thin sheeting under laboratory conditions. The horizontal dotted line indicates a plasticizer content at which the sheeting is hardened and a defect is obvious. The lifetime under laboratory conditions comes to 200 hours if plasticizers with small molecules are used. But the use of plasticizers with long chains results in a lifetime of 700 or more hours. This demonstrates the possibility of getting a very good lifetime only by the use of purposeful plasticizers. The test was made in the same way as discussed before. One side of the specimen was covered with a sheet of polystyrene and the other side was open to the air. The specimen was stored at 70C.

The increase of the modulus becomes a problem if the temperature in the surroundings goes down. The thermal coefficient of expansion of a PVC sheeting is rather large, $20 \cdot 10^{-5} 1/°C$. Therefore the sheeting is shortened by the falling temperature; this is nearly without effect, if the sheeting still is flexible. But a loss of plasticizer causes not only the increase of the modulus, i.e. the sheeting becomes hardened, but also, due to the loss of plasticizers, multiaxial shrinkages arise. By these shrinkages, stresses occur and they may cause damage by tearoff at the attachment points or rupture in the sheeting itself. That is why in wintertime the roof covering is extremely loaded. Therefore, it is desirable to know the values of these stresses as a physical and mathematical background for architects doing roof designs.

We measured the biaxial stresses with laboratory test equipment. Figure 8 demonstrates the influence of plasticizer content upon the arising stresses. The new and flexible sheeting with about 36 percent plasticizer shows at −30C only a force of 7.5 N/cm, but the shrinkage force in the same but hardened material with about 20 percent plasticizer is about 75 N/cm in width. This hardened sheeting has a shrinkage force at 0C of 2,500 N per meter width and 7,500 N at −30C. That means the attachment points of the roof covering are extremely loaded.

All these experiments were made with sheets without carriers. If the sheeting is supported by a carrier, e.g. a polyester fabric, the loss of plasticizer and the influence of ultraviolet radiation in practice, i.e. the aging, runs in the same way as described for the unsupported sheeting. However, one of the effects of plasticizer loss is different: the scale of shrinkage is only given by the fabric shrinkage, if possible, not by the film.

Another problem of lifetime is the aging of the PVC sheeting. It is not possible to separate the loss of plasticizer from the aging of the PVC. Aging in this meaning is the irreversible changing of properties depending upon the time. Aging is influenced by natural weathering, especially ultraviolet radiation. Depending on the angle of sunlight in Central Europe, up to 50 degrees north latitude ultraviolet radiation with a wavelength of about 300 nm will reach the earth's surface. The energy of this radiation is of sufficient intensity to split the polymer chains in the PVC. A wavelength of 300 nm corresponds to an energy of 399 kJ $\cdot$ Mol^{-1}. The bonding energy of an aliphatic C − C chain is 335 kJ $\cdot$ Mol^{-1}; i.e., it is possible to crack this bonding by ultraviolet radiation. The radiation is to be absorbed by the PVC. Technical PVC contains double bonds, or carbonylic bonds which are able to absorb radiation, and the C − C bond or the C − 0 bond (326 kJ $\cdot$ Mol^{-1}) may be cracked. This effects a degradation of the macromolecules and a shift of the molecular mass distribution, but in practice it needs some years before the effect is clear because the radiation penetrates only some micrometers into the film, as is seen in Figure 9. Therefore, it is useful to analyze not the complete material but only thin layers, beginning with the surface.

This attack of radiation only is possible if the sheeting is uncovered. A sheeting covered with gravel, about five cm thick, is protected against radiation. But the lifetime of the unprotected material is in practice often longer than the lifetime of a sheeting covered with gravel. The reason for this is the different mechanism in plasticizer loss. The surface of an uncovered sheeting is cleaved by the radiation after some years, even if the PVC is stabilized against ultraviolet radiation. A part of the macromolecules is degraded as described, but another part is so changed that the molecules are enlarged. These very large molecules are unable to solute the plasticizer and therefore the concentration of the plasticizer is enriched in relation to the PVC with original or lower molecular mass. The cleaved surface and the very large molecules act like an anticorrosive layer and prevent the loss of plasticizers.

In practice an uncovered sheeting of 0.8 mm thickness lost 8 percent of its plasticizers during a lifetime of 18 years. The same material covered with gravel lost 16 percent of its plasticizer within nine years and was defective. The reason is the direct contact of the surface of the sheeting surrounded with natural moisture, which is fixed by the gravel. It is not only the rainwater but a mixture of water, mud, microorganisms and oxygen which affect the loss of plasticizer. The surface of the PVC is undisturbed but hardened by the loss of plasticizer. It is impossible to reproduce this fact in the laboratory only with water. In practice the effect is very clear, and the so called protection layer is not a protection but disadvantageous for the lifetime of a PVC sheeting used for roof covering.

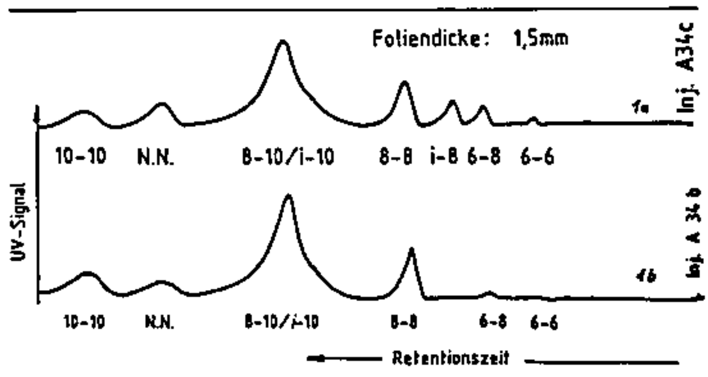

Figure 1 Loss of plasticizers with short chains

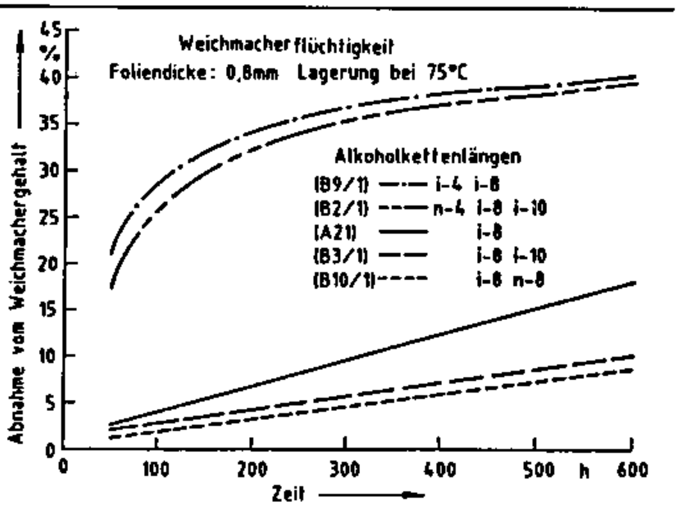

Figure 2 Volatility of plasticizers in correspondence to the structure

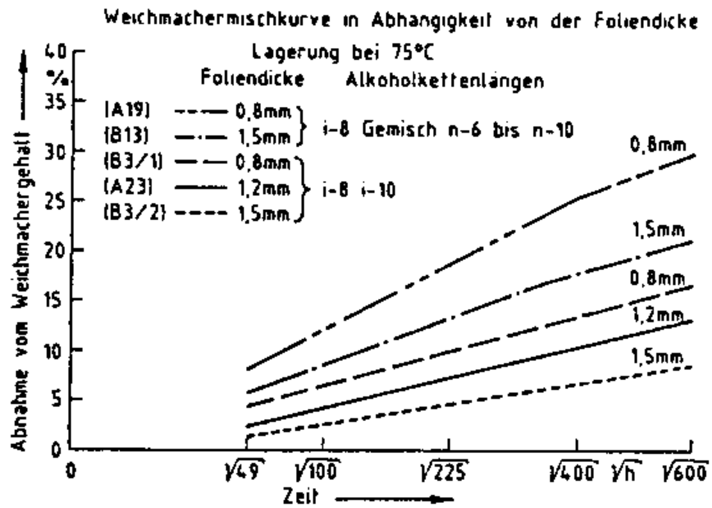

Figure 5 Migration of plasticizers in relation to the thickness of the sheetings

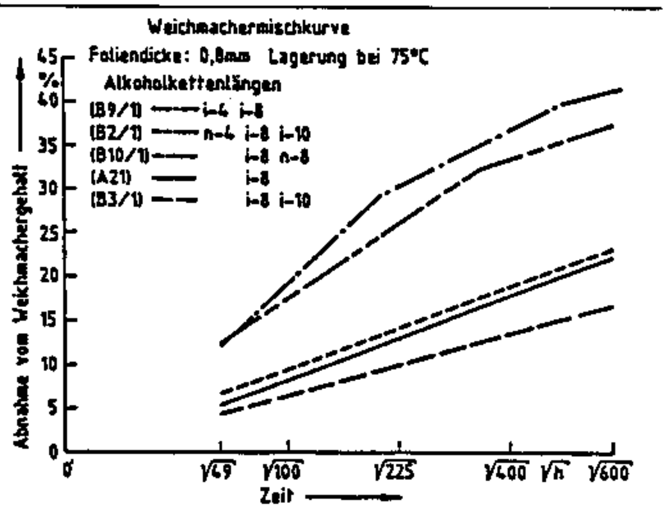

Figure 3 Migration of phthalic-esters; influence of chain-length and structure

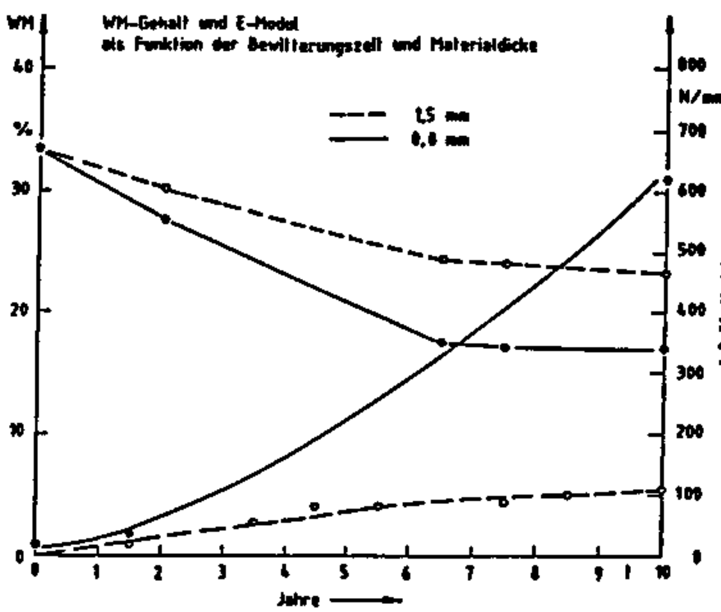

Figure 6 Loss of plasticizer and increase of the modulus during a lifetime of 10 years, corresponding to the thickness of the materials

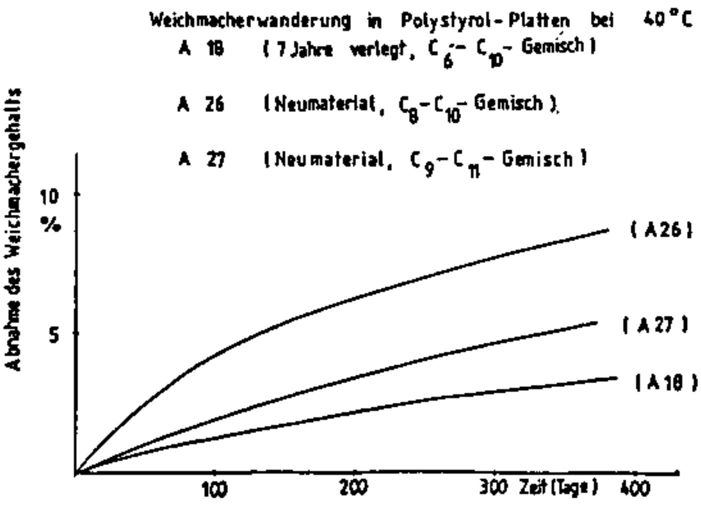

Figure 4 Migration of plasticizers into polystyrene at 40C

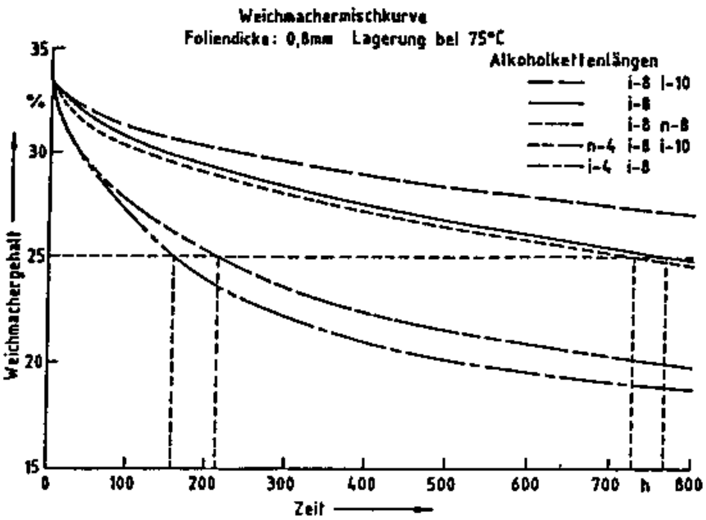

Figure 7 Structure of plasticizers and lifetime under laboratory conditions

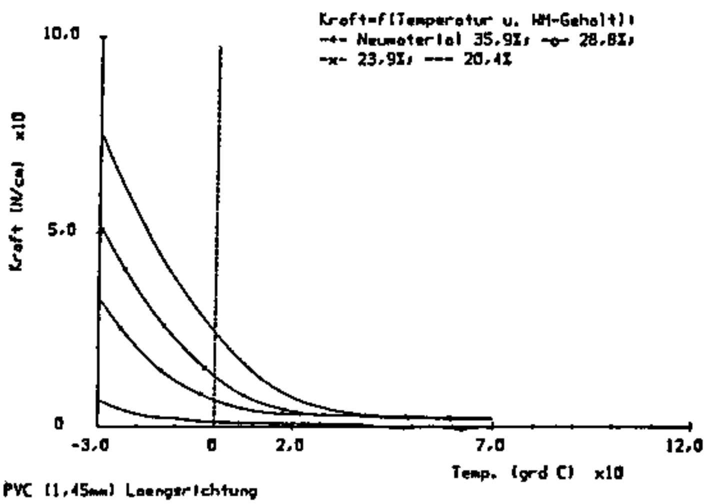

Figure 8 Shrinking force of a PVC sheeting in relation to the temperature

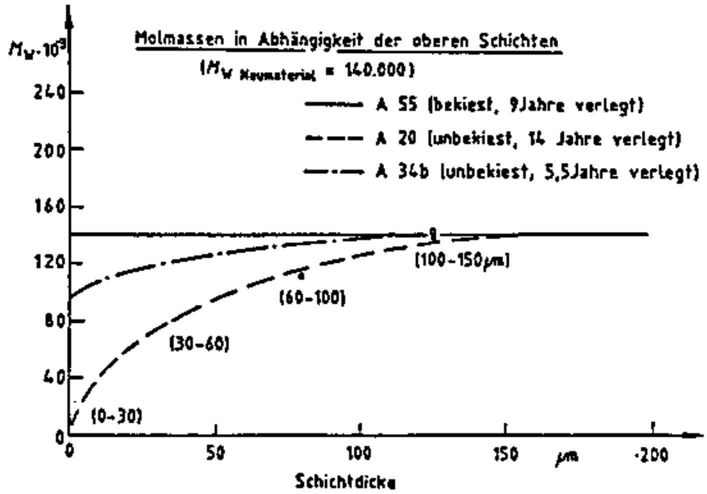

Figure 9 UV deterioration of PVC, penetration depth