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ID/WG.137/46
18 September 1972

Original: ENGLISH

United Nations Industrial Development Organization

Symposium on the Development of the Plastics Fabrication Industry in Latin America

Bogotà, Colombia, 20 November - 1 December 1972

CLIMATIC PROTECTION OF POLYETHYLENE FILMS[1/]

by

Valentin Ionita

Romania

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SUMMARY

CLIMATIC PROTECTION OF POLYETHYLENE FILMS 1/

by

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The fact that the high pressure polyethylene may be easily processed, may be extruded under the form of various thicknesses, having a good transparency and mechanical strength as well as a high chemical resistance, made this polymer to be preferred rather than other plastic materials especially in agriculture for light constructions.

Under the continuous and combined action of natural factors, the polyethylene film is usually degraded in less than a year.

The solar light comprises a maximum of energy in the range of ultraviolet rays, sufficient to break the chemical chains of C-C, C-H type. These radiations can cause the splitting of the polymer chain, leading to the formation of free radicals, whioh

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in the presence of atmospheric oxygen are changed in degrading products of C=O, C=C, O-H, O-O type, that are powerful ultraviolet light absorbing, capable to accelerate the distructive process of the film.

Due to this reason, the plastics must be stabilized against ultraviolet radiations by using substances which reflect ultraviolet radiations or substances absorbing ultraviolet radiations, producing the transformation of luminous energy in other forms of energy less harmful to the polymer.

The paper, based on some experimental results, demonstrate the favourable synergetic effect of substances admixtures "light absorber" and "free radical absorbers" in the case of low density polyethylene films.

The protective effect of these admixtures upon mechanical and optical properties of the polyethylene films is evidenced in comparison with the free additive films. Both the data obtained following a forced aging phenomenon and those following a prolonged action of the natural climate are presented.

This paper indicates some of the ways to be followed in view of extending the life period of polyethylene films especially in the agricultural field.

C O N T E N T S

I. INTR DUCTION

1. In the last years the numerous qualities of plastics determined their application on a large scale both in various industrial sectors and in agriculture (1). The properties of the macromolecular compounds which favour their application in agriculture can be enumerated as follows:

- reduced specific weight
- good permeability of polymer fillus to radiations
- thermal insulation comparable to that of glass
- liquid tight and poor permeability to gases
- good chemical resistance to agricultural products
- shock-resistant and obrasion proof
- high co-efficient of water descharge
- reduced cost price, in general.

2. Each plastic material totalizes a smaller or a bigger number of this amount of properties and their application represents important economic advantages due to a cheaper price of the products as compared to the traditional materials and cheaper costs of laying and exploitation.

3. Researches having in view the introduction of plastics in agriculture, concluded with the application of these plastics almost in all agricultural sectors namely:

a. Crops irrigation through furrows by means of mobile, flexible pipes made out of polyethylene.

b. Draining of salty soils by means of polyvinyl chloride pipes.

c. Impermeabilization of irrigation channels by means of plastics films.

d. Soil consolidation and stabilization with polymers.

e. Soil protection with polyethylene films and manufacture of light type solaria and greenhouses covered with polyethylene films reinforced with spun glass, polypropylene or polyamide fibres.

f. Protection of tower silos with plastics films.

g. Manufacturing of most various packages and especially polyethylene bags for fertilizers.

4. The mostly used plastics in agriculture or under way of experimentation are: polyethylene, polyvinyl chloride, polystyrene, polyester resins, methyl polymethacrylate, phenolformaldehyde resins carbamide resins.

5. The rapid growth of plastics production during 1960 - 1970 is to a larger extent due to their application in agriculture, as shown in Table I.

Table I

Plastics production in the world

(thousands t/y)

Type of plastic material	1963/65	1969	1975	1980
Polyethylene	2.446	6.432	16.172	32.163
Polypropylene	226	1.223	3.488	7.701
Polyvinyl Chloride	2.673	5.481	11.280	19.615
Polystyrene	1.268	2.944	5.662	9.603
Other thermoplastics	1.223	2.401	4.666	8.788
Thermal resistance plastics	4.077	7.384	13.227	20.793

6. Quite remarcable is the growth of polyethylene production by more than 10 times, of which the high pressure polyethylene has the major weight and more than 70% is used in agriculture. It can be confirmed that agriculture stimulated this important field of the chemical industry as it did with the petrochemical industry or with the inorganic salts.

7. The fact that high pressure polyethylene may be easily processed, may be extruded as films of various thicknesses, having a good transparency between 5-13%, a high mechanical strength between 130-180 kgf/sq.cm. and a high chemical resistance, made this polymer to be preferred to other plastic materials especially for light constructions in agriculture as solaria, fodder storages, storages for corn cobs a.s.o.

8. The common deficiency of all plastics resides in their relatively high speed of aging.

9. Polyethylenes of a paraffin structure are somehow advantageous as compared to othe plastics, but the con inuous and combin i action of the natural dynamic factors (oxygen, ozone, ultraviolet, infra-red radiations, humidity and pollution agents) usually degrades the polyethylene film in less than a year.

10. Degradation under the action of light is generally a photo chemical reaction, the speed of which is proportional with the absorbed quantity of solar energy and it depends on the photo chemical sensitivity of the material.

11. In the field of ultraviolet rays the solar energy comprises a maximum of energy, which values between 50-100 kcal, are sufficient to split many chemical chains as C-C, C-H, C-halogen. These radiations can cause polymer chains splitting by forming free radicals which in the presence of atmospheric oxygen are transformed in degrading products of C=O, C=C, O-H, C-O type. These are powerful ultraviolet light absorbing, capable to promote the distructive process.

12. This is the major reason for which plastics must be stabilized against ultraviolet radiations, either by substances that reflect ultraviolet radiations, before their penetration in the polymer mass or by ultraviolet radiations absorbers, which transform the light energy in other types of energy less impairing to the polymer.

13. The ultraviolet absorbers of agricultural films must possess a series of properties, especially a good compatability with the polymer, light and heat stability, a reduced evanescence, and a chemical stability towards the polymer. They should also avoid colouring or modifying the transparency of the plastic material.

14. There have been found numerous chemicals to meet these requirements. The most important chemical agents are the followings :

a. Benzoquinone compounds

b. Esters of salicylic acid

c. Resorcinol esters

d. Coumarin

e. Substitution derivate of acrylonitrile

f. Indole compounds

g. Compounds of the cyanic and triazinic acid.

15. For cases where the film transparency is not required, ultraviolet absorbers like carbon black and zinc oxide can be used, the latter being the most efficient inorganic absorbent.

16. By mastering the polymers degradation mechanism it was possible to increase the efficiency of the stabilizers synergetic admixtures, each component inhibiting a certain distructive process. The application of certain types of stabilizers is often determined by their price (3).

17. In general, the plastics degradation process leading to reticulation, chain splitting and formation of substances with oxigenated functional grouping is considered to be of a radical type, and in the case of polyetylene it can be represented as :

a. Initiation

$$R - H + O_2 \xrightarrow{)} HO_2^{\cdot} + R^{\cdot} \quad (1)$$

$$AH + O_2 \xrightarrow{)} HO_2^{\cdot} + A^{\cdot} \quad (2)$$

$$ROOH \longrightarrow RO^{\cdot} + OH^{\cdot} \quad (3)$$

$$2ROOH \longrightarrow RO^{\cdot} + RO_2^{\cdot} + H_2O \quad (4)$$

b. Propagation

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} \quad (5)$$

$$RO_2^{\cdot} + RH \longrightarrow ROOH + R^{\cdot} \quad (6)$$

c. Chain transfer reactions

$$RO_2^{\bullet} + AH \longrightarrow ROOH + A^{\bullet} \quad (7)$$

$$A^{\bullet} + RH \longrightarrow AH + R^{\bullet} \quad (8)$$

d. Cessation Reactions

$$A^{\bullet} + RO_2^{\bullet} \longrightarrow \text{stable products} \quad (9)$$

$$2A^{\bullet} \longrightarrow \text{" "} \quad (10)$$

$$2RO_2^{\bullet} \longrightarrow \text{" "} \quad (11)$$

18. Shelton mentions at least five different groups of oxidation inhibitors, that react through various inhibiting mechanisms (4) namely :

a. Peroxide decomposition

b. Metal deactivator

c. Light absorbers

d. Innibitor revivifier

e. Radical absorbers (Radical breakers).

19. More common antioxidants belong to the cathegory of light absorbers.

2o. On the basis of some experimental outcomes, the favourable synergetic effect of "light absorbing" and "free radical absorbing" admixtures is demonstrated in the case of low density polyethylene films having a M.F. I-2 and a viscosimetric molecular mass M = 35.000.

21. The protective effect of these admixtures is rendered evident in comparing a free additive polyethylene film with a ultraviolet absorbing one in a ratio of o,3%. To The film admixed

with 0,3% antioxidant, an accelerated chain breaker was added in two concentrations : 0,1% and 0,3%. The exposure of the samples was made in a Xenostat 450, and the effect of ultraviolet radiations was combined with 80% humidity and air circulation.

22. Sample exposures were also performed in a natural sea climate and an industrial one.

The results obtained are shown in figures 1-5.

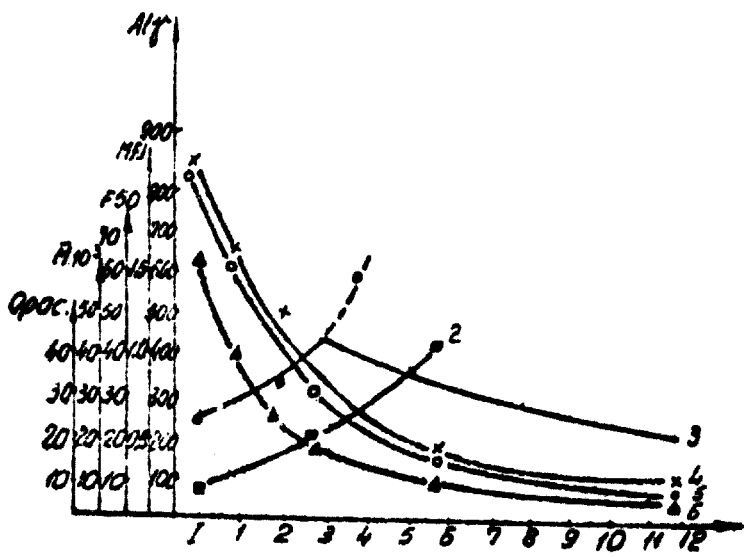


Fig. 1. Time variation of the properties of a polyethylene sample exposed in a natural climate for 12 months.

1. M insoluble; 2. opacity; 3. M soluble; 4. MFI; 5. elongation at break; 6. F.50.

23. Figure 1 shows the variation in time of the properties of a polyethylene sample exposed in a natural climate for a period of 12 months. A conspicuous deterioration of the mechanical and optical properties is registered, for instance elongation at break is 7 times reduced (curve 5) in less than six months. It is also observed that an increase of high molecular weight structures takes place during the first period of exposure (curve 1) while an increase of the procentage of low molecular weight formations occurs about three months later.

24. These results obviously indicate the necessity to protect the films exposed in a natural climate. Main changes take place in the first three months :

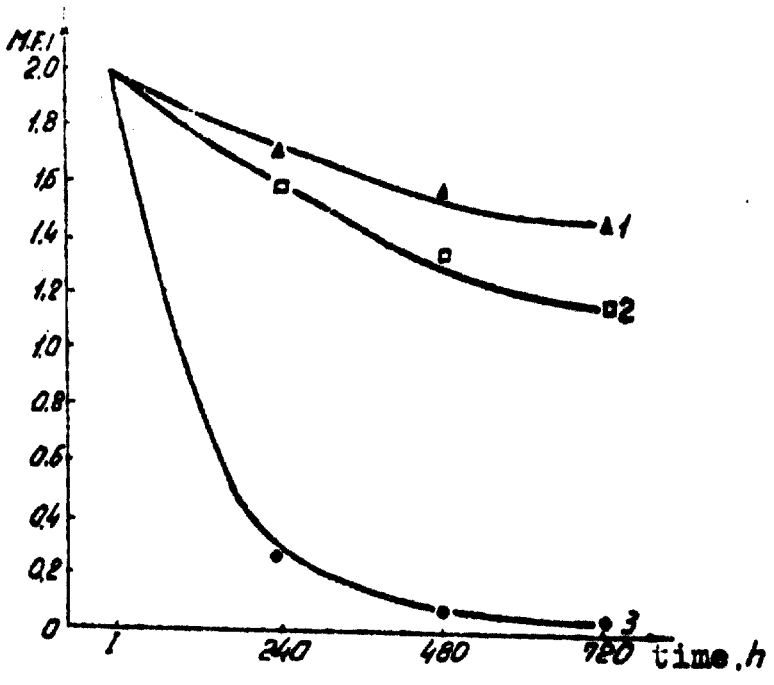


Fig. 2. Time variation of the *M.F.I. of samples* exposed in a xenostat 450; 0,3% ultraviolet absorber.

1. D.O.B.P.; 2. Tinuvin ; 3. Blank assay.

25. Figure 2 shows the variation in time of the melting flow index, for samples admixed with two types of 0,3% ultraviolet absorbers as compared with the blank assay which was untreated. The exposure was carried out in a xenostat 450. 720 hours after the exposure, the melting flow index of the untreated sample is reduced almost to zero (curve 3) and the sample admixed with D.O.B.P. changed from 2 to 1.5 (curve 1) and to 1.2 (curve 2) in case of Tinuvin.

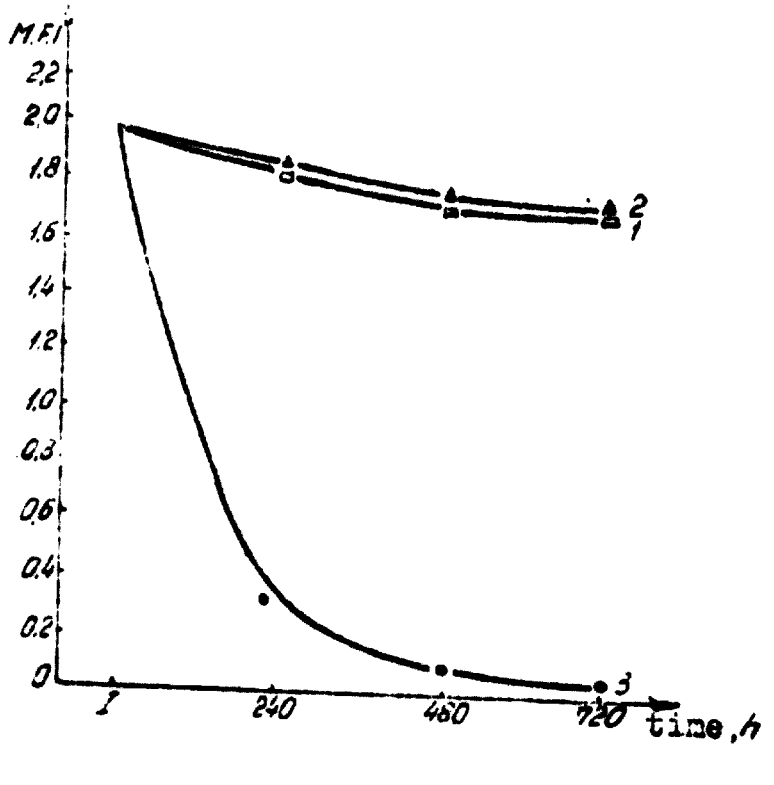


Fig. 3. Time variation of the M.F.I of samples exposed in xenostat 450, 0,3% ultraviolet absorber, 0,3% Santanox.

1. Tinuvin + Santanox; 2. D.O.B.P. + Santanox;
3. Blank assay.

26. Figure 3 shows the time variation of the flow melting index for samples admixed with equal ratios of 0,5% ultraviolet synergetic absorbers (Tinuvin + D.O.B.P.) and with free radical absorber (Santanox). The exposure was made in a xenostat 450. As shown in this figure, these synergetic admixtures, protect, in fact, completely the polyethylene film during those 700 hours of forced aging.

27. These results are also confirmed by the extended exposure of the samples in a natural climate as indicated in figures 4 and 5.

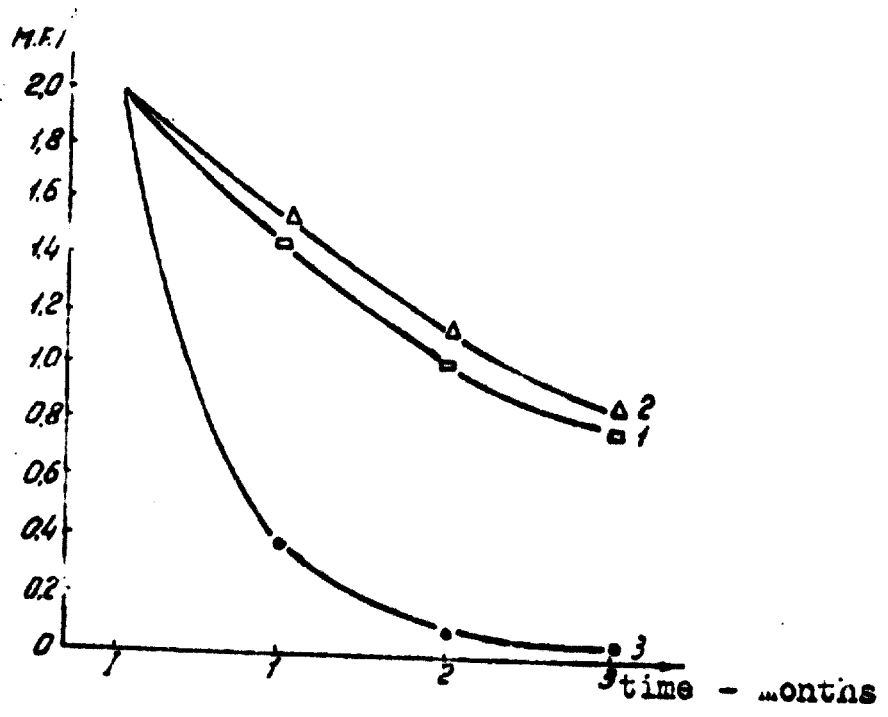


Fig. 4. Time variation of the M.F.I. of samples exposed in a natural climate. 0,5% ultraviolet absorber.

1. Tinuvin; 2. D.O.B.P.; 3. Blank assay.

28. The polyethylene samples admixed with ultraviolet absorbers in a ratio of 0,3% are gradually protected against the destructive action of the surrounding medium. Three months later the melting flow index decreases with 0.6 units both in case of Tinuvin and in case of U.V.S.P.

29. In comparing this figure with figure 2 it comes out that the natural climate acts more severely than the medium in xenostat 450.

30. The outcomes of an extended action of the natural climate can be really improved by using the synergetic admixture of Tinuvin - Santanox (fig.5).

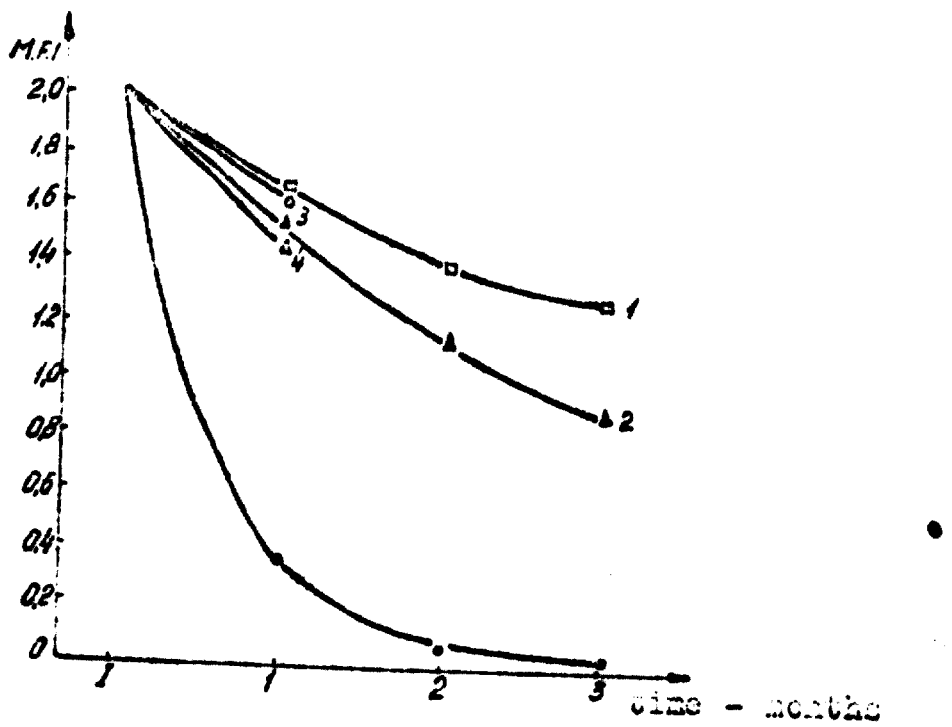


Fig. 5. Time variation of the M.F.I. of the samples exposed in a natural climate; 0,3% ultraviolet absorber, 0,1% Santanox.

1. Tinuvin + Sn ; 2. DCBP + Sn ; 3. Blank assay.

31. Thus from the figure 5 it can be seen that being exposed for a period of three months in a natural climate, polyethylene samples protected with the synergetic admixture Tinuvin - Santanox, decrease their melting flow index with 0.6 units.

VIII. CONCLUSIONS

32. Based on the data presented and the accumulated experience it can be confirmed that the exploitation period of high pressure polyethylenes admixted with ultraviolet absorbers and even better with ultraviolet synergetic absorbers (breakers of increased chain reactions) is extended by 300% as compared to the untreated polyethylene.

33. By using a Hungarian ultraviolet absorber "HOB" in a ratio of 0,3% together with Staro L/TP on an industrial batch of agricultural film we have obtained good results similar to those obtained in case of Tinuvin and D.O.B.P.

34. Optimum results are noticed by using 0.3 procent of ultraviolet absorber and a concentration of the free radical absorber of 0.1 - 0.3% as towards the polyethylene.

35. The optimum ratio of the two components depends on the structure of the respective substances.

IX. SUGGESTIONS

36. The common deficiency of plastics is the relatively high speed of aging under the combined action of the natural climatic factors. For the case presented, namely polyethylene films exposed to outside factors for a longer period the followings are recommended.

37. Stabilization of polyethylene films with synergetic admixtures of ultraviolet absorbers (various organic components of Tinuvin DOBP and HOB type) and of free radical absorbers (antioxidants of Santanox, Topanol and Armid - type a.s.o.).

38. The use of various additives, as polyethylene stabilisers obviously depend on their cost price and the field of application. In cases where the optical qualities of the films are not important, carbon black and zinc oxide are recommended.

BIBLIOGRAPHY

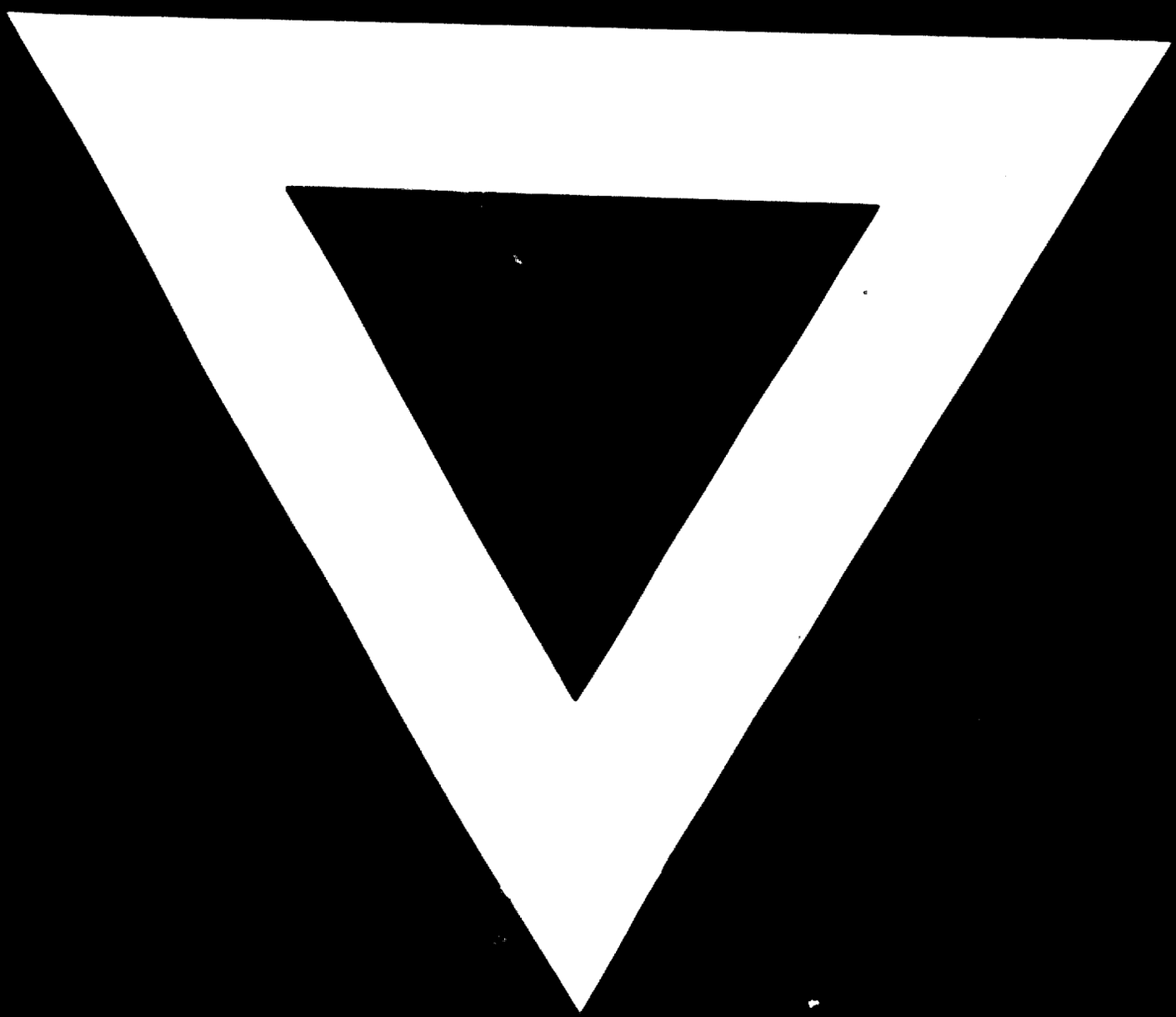
1. Dinu N., Wolf B., Ionescu M., Plastic Materials (Romania) Nr.1, 1964. p.29

2. Dinu N., Wolf B., Mohr F. - Plastic Materials (Romania) Nr.6, 1965. p.393

3. Deanni R., Polymer Engineering and Science 10, Nr.10, 1970. p.228

4. Encyclopedie of Polymer Science and Technology 2, p.171.

5. Moncea C., Sinchievici E., Parausanu V. - Plastics Materials (Romania) Nr.4, 1971. p.195



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