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CONSOLIDATION OF CAPACITY OF INSTITUTE OF FOOD TECHNOLOGY THROUGH CREATION OF A NATIONAL FOOD PACKAGING CENTRE

DP/BRA/82/030

BRAZIL .

Technical report: Flexible Materials in Packaging*.

Prepared for the Government of Brazil
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of Bohdan Czerniawski,
Expert in Flexible Packaging Materials

United Nations Industrial Development Organization
Vienna

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3. SUBSTANTIVE SECTIONS

1. INTRODUCTION

1.1. Project background

Packaging demand in Brazil is growing very fast, specially in the food packaging field.

Besides the increasing consumption of packaging materials, the technological aspects are becoming more and more important.

ITAL's Packaging Section has followed the demand of Brazilian Industry in the way that, since 1982 it is expanding its activities and facilities through an integrated program to put into operation a Food Packaging Center (CETEA) under the sponsorship of the Government of the State of São Paulo, the Brazilian Government (FINEP - EMBRAPA) and the United Nations Development Programme (UNDP), through the United Nations Industrial Development Organization (UNIDO).

At the moment the Packaging Centre comprises 15 graduate specialists (4 M.Sc. and 11 B.Sc.), 12 technicians and 6 general supporting staff.

The UNIDO/Brazil Food Packaging Center Project is identified as the Project BRA/82/030 with the duration of five years.

One of the more important activities of this project is the development of the CETEA'staff through training in packaging technology.

This training should enable the CETEA staff to fulfill the main objective of the Food Packaging Center - support to packaging and food industry in Brazil.

1.2. Objectives of the Mission

According to the job description, following activities were developed during the Mission:

1- Short courses and internal seminars related to flexible materials used for food packaging including fabrication, quality control tests, machinability and quality improvement;

2- Appraisal of the main equipment already available in the Center and specification of the complementary for this laboratory to be used for food packaging;

3- Training of the personnel of the Center on the equipments that already exist in this field;

4- Visit to the industries, producers and users of flexible materials in order to detect the main problems and to analyse the present demand for these materials in Brazil;

5- Analysis and orientation of the present and future projects of flexible packaging at CETEA.

6- Seminars and talks to the food and packaging industries regarding the tendency of flexible packaging for food, the main quality control tests and quality improvement of the flexible materials.

2. SUMMARY OF FINDINGS AND RECOMMENDATIONS

2.1. Recommendations concerning CETEA staff

On the basis of two months co-operation with the whole group (Internal Seminars) and with the Plastic Packaging Area in particular, it is quite evident that the management of the Center was able to gather young people full of energy and enthusiasm for the area in which they are working.

Taking into account the relatively short time of professional experience, they have already quite a good background for further development.

During individual conversations, it was observed that the majority of the group is very much engaged in continuing their studies on higher level specialized University's Departments e.g. in Michigan and Rutgers in USA or in München in West Germany.

This enthusiasm should be used properly and support from ITAL management would be highly appreciated.

At present time for the group of 33 persons only one secretary is employed, working as a typist and secretary of UNIDO's project co-ordinator - CETEA's manager.

As a result, very often gratuated personnel, instead of concentrat themselves on solving their professional subjects, are engaged in administrative types of work .

The additional employment of a person on secretary level, would be conducive to the efficiency of the conducted work. works.

From the beginning of the UNIDO project three persons left the group and nobody was employed in their place.

This situation cannot be considered as a continuing tendency. However, in order to ensure further proper implementation of the project, the reasons for these leavings should be carefully analysed and actions taken for maintaining the staff at least on its present level.

2.2. Recommendations concerning the projects of the Plastic Packaging Group

More detailed suggestions and recommendations concerning particular projects are given in section 3.5. In this section only more general type of recommendations will be presented.

On the basis of the discussions of the projects being or intended to be conducted, more complex approach, in these projects was highly recommended.

First of all, it seems necessary that enough time should be devoted to preliminary studies and collecting necessary information concerning the subject and its analysis, prior to experimental work start .

In the case of shelf-life of packed products with use of different materials under consideration, some consequences of future application of these materials should be taken into account, these include :

- type and degreee of required protection;
- availability of the materials on the market and their already known properties;
- conditions of use of the materials and the package, in the whole chain of storing, transportation and selling;
- behaviour of the materials in the conditions of hazards, which can take place in practice.
  (for simulation of the handling hazards, it is recommended to check also the shelf-life of the product packed with use of the material, subjected to standard crushing). Before eventual buying of Gelbo-Tester, the system presented in appendix 5 and demonstrated to the Plastic Packaging Group, can be used.

- packing, filling and sealing systems possible to apply in the analysed case; including the degree of adjustment of the analysed materials for packing machines.

- economic consequences of the use of particular materials under consideration.

- sales appeal possible to achieve and the degree of its meaning in the analysed case.

All these factors can have essential meaning for the selection of materials used in the investigations.

There is no doubt that elaboration and improvement of testing procedures, including control systems of possible contaminations of the food by ingredients of the packaging materials, should constitute an important area of the subjects conducted by CETEA staff. But besides this area, the subjects of a very practical nature with a high probability degree for implementation into the practice, should have evident participation in the CETEA's research program.

Optimization of the packaging solution in justified cases is a good example of this type of work. Some background given for packaging staff in packaging economy should prove to be very usefull in this case.

All this should strengthen CETEA's co-operation with the packaging and food industry.

In the adviser's opinion, this type of approach should be taken into account in some of the projects already started. The project to study dried milk packaging can serve as a good example.

2.3. Co-operation with packaging and food industry

Strengthening of co-operation with industrial organizations should prove to be natural consequence of the type and quality of the projects being conducted. This was discussed in the section 2.2. It was evident and it was proved during the common visits, that some of the industrial organizations are interested to start or to expand co-operation with CETEA staff.

The future of the co-operation with industry depends, of course on the degree in which CETEA staff is able to enlarge its experience in packaging technology and in general knowledge. There exist some fields in which co-operation with highest technical level companies is also possible,Taking into account the quite well equipped CETEA laboratories, these companies should prove to be interested in inter-laboratories studies. Some suggestions in respect to this, were given in the section 3.4.

2.4. Some suggestions concerning present use of flexible materials

On the basis of observations of the market of the towns of São Paulo State and of some other big cities many flexible packaging materials may be apt for high level solutions.

Gravure printing used on a wide scale and development in the ink making provide specially spectacular effects of majority of flexible packaging. As it was indicated in the section 3.4. , carefulness of appearance, however, is not always in agreement with proper use of the material possibility.

It seems logical that besides the production of laminates (sandwich printed prior to metallisation), where mainly appearance is provided , production of surface-printed metallised laminates should be initiated and/or widespread. Only in this case, all possibilities of barrier properties of this kind of laminates can be exhausted.

The system of ground coffee packing with use of metallised laminates should be studied more carefully. The vacuum or neutral gas packing constitute e only solution for protection of this type of product.

Properly used metallised laminates, without perforation of the bags, are the most suitable materials for using in these systems.

The system used on the market nowadays does not protect the coffee against oxidation during its period of guarantee. This was checked by the adviser personally when he bought, in a big supermarket, absolutely undrinkable ground coffee packed in metallised laminate.

There is a real need for improvement of frozen fish packaging. The packing system and probably the freezing chain does not provide proper protection of the product. Folding carton boxes used in this case are swelled on internal or external side, and the product indicates the oxidizing effects. Some suggestions about this were given to the Plastic Packaging Area'staff.

2.5. Quality control of flexible materials and packaging

Taking into account that CETEA's laboratories are relatively well equipped, the adviser paid more attention in his work to the expansion of using the equipment already existing than on writing specifications for new equipment .

In the last case, suggestion was only made for buying a Gelbo-Tester to simulate hazards during the handling procedure.

The adviser also participated in writing specifications for a new strength measuring machine.

Recommendations given as far as wider use of presently available equipment is concerned and some simple adjustments possible to realise in local workshops are described in the section 3.3.

3. SUBSTANTIVE SECTIONS

3.1. Short Courses and Internal Seminars on Flexible Materials used for Food Packaging

Internal seminars were arranged for the whole staff of CETEA.

Programme of the course is given in Appendix 1.

During this course, production, properties, application and quality control of flexible packaging were discussed with special attention paid to interdependence between manufacturing parameters and properties essential in packaging applications.

During one month course the seminars took place three times a week, 3 hours each.

After being printed, before each seminar the full text of particular lecture was delivered to all participants.

An example of one of 14 topics prepared for the seminars is given in Appendix 2.

This system allowed more active participation of the whole group, including those who had some difficulties in understanding spoken English.

Upon the basis of the supplied materials, participants more advanced in the subject and foreign language prepared the others who encountered the above-mentioned difficulties for participation in the seminars.

3.2. Appraisal of the main equipment already available in CETEA

Generally speaking CETEA's laboratory in the field of testing flexible materials is relatively well equipped.

There is real need, however, to install a new strength measuring machine. The presently installed "Instron" not only constitutes an old model but also is not equipped with some of the accessory necessary for testing flexible materials. Because the machine presents an old type, not produced any longer, some of the accessory may not be available anymore. In co-operation with the Plastic Packaging Group, the type of the equipment and necessary accessory for proper exploitation of the machine were specified.

Taking into account the significant meaning of "shelf-life" investigations in activities of the Plastic Packaging Group for more realistic evaluation of the materials, it was recommended to buy the equipment providing the possibilities to simulate the hazards intereacting flexible materials during their handling. This type of equipment is known as a Gelbo Flex. The tester is produced by the Ameresco World Corporation (Montclair, New Jersey). The model with the engine is adjusted to the voltage 110 Volts and equipped with the strokes adjusted for testing aluminium foil laminates, and metallised and other types of laminates.

3.3. Training the personnel of the Center in use of already existing equipment:

During the adviser's assignment some recommendations were made as far as the use of presently available equipment is concerned. This included also some simple adjustments possible to realise in local workshops and would provide for the extension of testing possibilities.

The list of 14 subjects being discussed in this area and the tests conducted under the supervision or according to the adviser's suggestions are given in Appendix 3.

In the majority of cases the subjects were prepared and submitted in the way as it is presented in Apendices 4 and 5. These examples constitute measurement of elasticity modulus, method of standard crushing of the flexible laminates prior to water vapour permeability measurements, out-of-flatness measurements (given in specification for films used in dry bonding techique) - (Appendix 6) and some other tests described in specification of ready made laminates (Appendix 7).

Independently of the tests listed in Appendix 3 the values of the threshold for the solvents frequently used in production of flexible materials determined by the method of dilution factor , were also presented (Appendix 8).

Taking into account that food product contamination constitutes one of the most important topics of the Packaging Centre, the list of polymerization residuals and additives used in production of flexible materials was elaborated.

This list is presented in Appendix 9.

3.4. Visits to the Manufacturers of Flexible Materials and Research Laboratories

Together with Plastic Packaging Area visits were paid to six factories being the manufacturers and/or converters of flexible materials. For better use of these visits the participants' group was prepared by the adviser through discussions of specific features of the materials and technologies of their making. These discussions took place prior to the particular visit and were often held in the car on the way to the factory.

Votocel, located in Votorantim (SP), is one of two manufacturers of cellophane, only approximately 65% of the present production capacity amounting to about 10,000 tons, is used. Vinylidene copolymer coated grade constitutes 35%, the rest belongs to nitrocellulose coating. In Votocel new installation is just completed for production of coextruded OPP film (WOLF - West Germany Company license) at the yearly planned production of 3.500 tons.

Though this situation is typical for many cellophane producers in all over the world, Votocel's managing staff has its justification to be optimistic concerning the future of their cellophane; this is a result of an exceptionally good solving of air- and water-pollution problems, gradual transfer of energy sources based on the availability of coal and other raw materials (the use of cellulose based on eukaliptus trees of exceptionally fast growth in the conditions of Brazil).

Votocel's management is especially interested in future cooperation with CETEA'staff, taking into account the need of proper use of the new equipment which will be installed in the division of polypropylene film making.

"Polo", located in Varginha, MG, is one of two manufacturers of oriented polypropylene films (production scale 6000 tons/year).

In Polo's technology heat sealing properties of OPP films are achieved due to some additives to basic polypropylene resin. This type of material has limited range of application (40% of the whole production is used for cigarette over-wrappings) because the heat seal strength of this type of OPP films is not acceptable in the case of majority of form-fill-seal systems. The company intends to adjust one of the existing lines (tubular orientation process) for production of coextruded OPP films. This allows to expand the range of present applications, including form-fill-seal systems.

Polo's laboratory is well equipped. Their own method for hot-tack measurements and the static discharging system prior to slip measurements are worthwhile of additional interest for CETEA'staff.

ALCAN, located in Santo André - SP, is the smallest between three Brazilian manufacturers of aluminium foil. In the same company conversion of Al-foil is conducted and is presently expanded due to installation of a modern, well-equipped and separately located new division.

The quality control system conducted in a very detailed form and according to requirements of standards, submitted by the individual customers, is worthwhile to be a subject of additional interest for CETEA'staff.

Among converters of flexible materials, visits were paid to TOGA, EMPAX and POLYFILM.

TOGA, located in São Paulo, is the biggest converter of this type of materials in Brazil (26% of the whole tonnage of converted flexible packaging that corresponds to the value of the production: US$56 million/year). Consumption of some of the raw materials used for further conversion amounts per year to:

Al-foil - 1700 tons
PE - 1200 tons
PETP film- 500 tons
OPP film - 350 tons
cellophane - 200 tons
surlyn - 5 - 10 tons

Almost all basics techniques are applied for production of many types of composite materials. These include dry, wet, wax and extrusion bonding; coating with use of dispersion; hot melt, extrusion; solvent based heat and cold sealable coating; gravure printing using up to eight colours and metallization.

Modifications of the paper for further printing and laminating is another big area of the company's activities.

The share of TOGA production on brazilian market in 1984 was the following:

Structure	Application	% participation
1- PAP/PE	wrapping	5%
2- Al/PE	cigarettes	18%
3- CELO/PE/CELO	biscuits	3%
4- Al/PAP/PE	wrapping	14%
5- PAP/PE/Al/PE	juices	44%
6- PAP/HOT MELT	soap	85%
7- CELO/PE	pastry	3%
8- BOPP/PE/BOPP	biscuits	4%
9- PET/MET/PE	coffee	57%
10- Al/PE	lids	7%

TOGA's laboratory is especially well equipped, not only in quality control equipment, but also in pilot scale coating, laminating and printing machines. At present time it is probable that such a high level company will be more interested in conducting, in selected areas, interlaboratories testing, than in any other way of co-operation with CETEA.

On the other hand TOGA's laboratory is mainly involved in quality control and because of that the company should be interested in co-operation with high level Research Institute able to solve their research problems.

The share of the EMPAX(Santo Amaro-SP), another visited converting factory, in tonnage of converted flexible materials is equal to 12% (the second after TOGA). The company produces a wide range of different composite materials, though not so many different techniques are applied as in TOGA. Their metallised laminates are based on exterior suppliers of metallised substrates.

The company seems to be interested in co-operation with CETEA. At the present level, support from the side of the Food Packaging Centre to this company is possible.

POLYFILM (São Paulo - SP) is a small scale company being a manufacturer and converter of single flexible films (e.g. LDPE, HDPE, PP, PA) and some laminates (coextruded PA/PE).

The company's laboratory is used for quality control and is trying to solve the existing technical problems themselves. Nevertheless with more active approach from both sides, co-operation with this company seems to be possible.

On the basis of the visits to companies, the general conclusion can be made that in each case special attention is paid to the appearance of the package. High quality of the printing should be aimed at. For achieving this quality, the principle of applying own technology of the inks production (with use of delivered components) is quite common.

The gravure printing assuring specially spectacular effects (with possibility of eight colors) is the most frequently used technique.

It should be underlined that printing is often realised on gravure presses produced in Brazil. Gravure cylinders are often produced in place even in smaller scale companies (e.g. Polyfilm).

Carefulness for appearance not always remains in agreement with proper use of material possibility. The system of applying metallised laminates can serve as an example. In the case of metallised PETP/PE laminates, as a rule, reverse printing of PETP films is prior to metallisation of the film. This system causes 5-6 times decreasing of barrier properties possible to achieve with the same type of laminate containing PETP film surface printing. Upon the basis of the discussions in the converting factories, conclusion can be made that some converters are doing it with full consciousness, but some of them, who don't realize the metallization process in their place, are not aware of that.

During the adviser's assignment visits were paid to the Technological Research Institute - IPT, located in São Paulo - SP (Cellulose and Paper Division and Plastic Division) and to the laboratory of the Brazilian Association of Corrugated Board - ABPO. In each case the group was acquainted with the equipment and the tests conducted in each particular place. It seems that especially good conditions exist for co-operation with the Cellulose and Paper Division of IPT.

3.5. Analysis and orientation of the present and future projects of flexible packaging at CETEA

Among the works already done, the following topics were discussed:

- Consumer packaging for frozen food of animal origin;
- Behaviour of crystal sugar during storing;
- Consumer packaging for already cleaned carrots;

Among the projects being conducted or predicted for the future the following topics were discussed:

- Replacement of tin cans for dried fat milk powder by the use of flexible high barrier material;
- Protection of delicate fruits (parsimons) during storing, transportation and selling;
- Quality control of metallised flexible laminates;
- Gas chromatography in control of the products of oxidation of polyethylene.

Short comments on each topic is given below.

3.5.1. Discussion of some of the projects already done

<u>Consumer packing for frozen food</u>

Frozen fish packing system with use of folding cartons was generally criticised. In all analyzed versions the product is not properly protected against oxidation. Some recommendations were given according to construction of the package and composition of the material.

Behaviour of crystal sugar during storing

Two different approaches were recommended in this type of works.

For research purposes for control the speed of the changes of water content in dependence of the humidity, the possibility existing for applying close circuit with required relative humidity and with the use of spiral type quartz microbalance, was indicated.

For practical solving of this problem, the material providing protection against water vapour penetration should be used. Optimization of this type of package, including technical and economic aspects of proposed solutions can be considered as a task for CETEA paper packaging specialists.

Consumer package for already cleaned carrots

As a result of this work, portion type consumer overwrap for long-term (even up to half a year- time protection) was selected presuming that indicated temperature and humidity would be provided.

It was suggested that in this type of investigations prior to shelf-life studies, detailed information should be collected concerning the practical possibility of storing, transportation, prepacking and so on.

The analysis of this information can have an essential influence on creation of the research program of shelf - life testing.

It can prove to be justified for example to store the product in a collective type of transit packaging, with its prepacking directly before selling. In this case, a different approach to the shelf-life testing will be made.

3.5.2. Projects being conducted or planned for the future

Replacement of tin cans for dried fat milk powder by the use of flexible barrier materials

As a result of an analysis of the results achieved and the discussion held with a RHODIA S.A. representative, who supplied the collection of the materials for preliminary control of barrier properties, conclusions were made concerning the choice of the material for final shelf-life testing.

They include met PETP/PE (12/70) and PETP/Al/PE (12/12/50). On the basis of the results presented by the authors some were classified as essential. These included:

- negative influence of reverse PETP film printing prior to metallisation for barrier properties of the material;

- non essential meaning of the substrate thickness for barrier properties after metallisation:

- negative influence of too high stiffness for machine running in vertical form fill seal system;

- economic aspects of the use of different combinations of flexible materials.

Recommendations covering all above mentioned factors were given.

Protection of delicate fruits (parsimons) during storing, transportation and selling

It was suggested in preliminary studies of this project to concentrate on finding the type of packing for shelf-life testing, which could be taken into account for further application in practice. One example of such a solution was presented, based on the use of consumer folding boxes placed in one layer in flat with open sides wooden or plastic box, and protected with properly selected films.

A suggestion was made for the use of polyethylene film with perforation planned on an experimental basis. The construction of one layer type transit boxes should allow to place them one over another.

Quality control of metallised materials

Taking into account one new project which is just starting at CETEA, concerning metallised films and laminates, measurement systems of Al layer thickness in these materials were discussed with the Plastic Group.

During the visits paid to local industry it was observed that though quality control tests include resistivity and optical density, the real values of Al thickness are not known.

It is well known that optimum value of Al thickness should not be exceeded because it involves not only unncecessary increase of Al consumption, but also it influences negatively the adhesion of Al to metallised films.

On the other hand, CETEA is not yet equipped with useful devices for checking Al layer.

The adiver's recommendations concerning the choice of the method used for this purpose was presented in the specially prepared report submitted to the Plastic Packaging Group and discussed during one of the Internal Seminars.

Practical tests were also made under the adviser's supervision. Though these types of tests are time-consuming and require high accuracy they allow to find a correlation with optical density measurements. Once this dependence is determined, further control can be based on optical density measurements.

Gas chromatography in control of the products of polyethylene oxidation

The system used in the Polish Packaging Research and Development Centre for anticipating the contamination of packed foodstuffs by odour of packaging materials was presented to the author of the planned project. The system proved to be effective in the case of solvent retention and its suitability in the considered case can be the subject of preliminary investigations of the considered project.

3.6. Seminars and talks to the food and packaging industries

The adviser participated in an external seminar for food and packaging industry and university specialists.

During this seminar the adviser prepared four papers according to the programme given in Appendix 10.

The result of the discussion with participation of the representative of Rhodia S.A. (production of polyethylene terephtalate film) is given in the Section 3.5.2.

PROGRAMME OF THE INTERNAL SEMINARS FOR THE PACKAGING CENTRE OF THE FOOD PACKAGING TECHNOLOGY INSTITUTE

Subject: Flexible Materials Based on Plastics in Packaging

I. Plastics and other materials combined with plastics in production of flexible packaging materials:

- basic polymers
- methods of polymerization
- compounds used in polymerization processes
- some basic features of polymers and basic terms used in plastics technology (e.g. rheology of plastics, glass transmission temperature, etc.)
- international coding system of different plastics
- trends in production and consumption of different polymers, including the Brazilian situation

II. Cellophane:

- present and future trends
- comparison of prices
- production
- structure
- regenerated cellulose modifiers
- properties of uncoated cellophane
- cellulose film modifications
- examples of special requirements regarding packaging machines

III. Polyethylene:

- consumption in packaging
- production
- polyethylene grades (classification and related properties)
- tubular film production
- flat film extrusion
- influence of the manufacturing process on film properties
- codes used for PE grades
- properties of LDPE films

- properties of LLDPE films
- properties of HDPE films
- PE treatment required for printing and lamination
- machineability of PE films

IV. Polypropylene films:

- forecast and production
- PP structure
- unoriented PP films (production, consumption, properties, applications)
- theory of orientation
- types of orientation
- production of oriented films
- properties of oriented films (coated and coextruded included)
- quality control
- applications

V. Some other modified polyolefines (e.g. ionomer, ethylene-vinyl acetate copolymers):

- structure
- properties
- applications

VI. Polyester (polyethylene glycol terephtalate, polycarbonate):

- production
- properties
- modifications by coating and laminating
- applications of uncoated films
- applications of coated films

VII. Polyamide films:

- classification of different grades of polyamide and their production
- properties of PA grades used for film production
- production of tubular films
- production of flat films
- relationship between technological parameters and properties of the film

- mechanical strength and thermal resistance
- barrier properties
- oriented PA films

VIII. Polyvinyl chloride films:

- production
- physical properties
- vacuum and pressure forming techniques
- trouble-shooting of thermoforming process
- construction of "blister pack"
- "skin pack" systems
- quality evaluation

IX. Polystyrene and cellular polystyrene films:

- high impact polystyrene
- biaxially oriented
- cellular polystyrene
- properties
- applications

X. Shrink films:

- statistics, general trends
- classification of thermoshrink grades
- exploitation properties
- shrinkability and shrink tension (measurement methods included)
- theory of thermal shrinkage
- production of shrinkable films
- thermoshrink films applications
    - direct overwrapping
    - vacuum packing
    - multipack forming systems
- grouping of the products for shrink packing
- protection of unit loads with use of thermoshrink films
    - palletised loads
    - loads without pallets
- heating systems

XI. Stretch films:

- comparison of stretch and thermoshrink films
- types of stretch films
- quality requirements
- overwrapping with use of stretch films
- types of trays used in combination with shrink and stretch films
- protection of palletised loads

XII. Flexible packaging laminates:

- general explanations
- classification of laminates
- lamination of ready-made films, wet and dry bonding
- laminates produced by extrusion and coextrusion coating
- laminates produced by extrusion and coextrusion lamination
- properties of laminates
- quality control of the films for lamination and ready-made laminates

XIII.Coextrusion systems:

- forecast and markets
- resin selection
- rheological properties
- adhesion between coextruded layers
- blown film coextrusion systems
- properties of coextruded films
- typical coextruded structures

XIV. Metallised flexible packaging films and laminates:

- consumption and forecast
- metallising techniques
- single ply metallised films
- metallised substrates (oriented PP, PA, PETP) and LDPE
- measurements of AL layer
- relationship - deposition of AL layer and barrier properties of metallised structures
- applications

APPENDIX 2

FLEXIBLE PACKAGING LAMINATES

GENERAL EXPLANATIONS

Terminology

Laminate is defined as any combination of different or the same plastic film materials or plastic plus non-plastic materials (paper, aluminium foil,cellophane) wherein each major layer is generally thicker than 6 µm. There is no upper limit to the possible number of plies, but two is the obvious minimum and one of these is usually thermoplastic.
Accepting such a definition one must accept also the fact that laminates may be formed not only by classical bonding of ready-made layers but also by extrusion and coextrusion coating and laminating.

Aim of Laminates Making.

The main aims of lamination are as follows:

- to provide combination of physical properties, which cannot be achieved by use of single plies,
- to provide this combination of properties in a possibly inexpensive way.

Taking PA/PE laminates as an example and refering to the table where mechanical and barrier properties of single layers are described it can be seen that the advantage of ready made laminate will be a result of:

- good mechanical strength, ability for thermoforming, resistance to high temperature, good barrier properties for gases and resistance to oil and greases, being characteristic features of PA films,
- low water vapour permeability, high heat sealing strength and relatively wide range of sealing temperatures and possibility of controlled slip characteristic of PE films.

Combination of both films into one material provides the package, suitable for packing a whole range of perishable goods, which would not have been distributed without use of this type of package. Due to combination of the properties of both plies, the material canbe deep drawing, allows to keep a vacuum in already made pouches for a reasonably long time and is resistant to some extent to thermal processing.

Classification of Laminates

Known laminates can be classified as follows:

- flexible laminates,
- semi-rigid and rigid laminates.

Flexible laminates in dependence of application can be classified as it is shown on the next page. In each classified group the example of laminate types is also given.

Most frequently used methods for production of laminates:

- lamination through use of adhesives and hot melts,
- extrusion coating,
- extrusion laminating,
- coextrusion.

CLASSIFICATION OF FLEXIBLE PACKAGING LAMINATES IN DEPENDENCE OF APPLICATION x/

- for packing the products requiring vacuum or neutral gas packaging
  - Thermoformable
    - PA/PE
    - PA/PP
  - Non-thermoformable
    - PETP/PE
    - PE/PVDC/PE
    - PETP/Al/PE
    - Cellophane/PE
- for the products requiring a different type of protection, but when vacuum or neutral gas packing is not necessary
  - Temperate barrier properties
    - paper/PE
    - glassine/PE
    - OPP/PE
    - Glassine/PVDC
    - OPP/OPP
    - AL/paper/PE
    - glassine/hot melt/PE
    - PE/Jonomer
  - High barrier properties
    - cellophane/Al/PE
    - PETP/Al/PE
    - PA/Al/PE
    - OPP/Al/PE
    - PE/PVDC/PE
- For liquid packing
  - PE/PE
  - PA/PE
  - PETP/PE
  - PETP/Al/PE
  - OPP/Al/PE
  - PE/PVDC/PE
- Adjusted for heat sterilization
  - PA/PP
  - PETP/Al/PP
  - PA/Al/PP
  - PETP/Al/HDPE

x/ only examples in particular groups are given.

Lamination of ready-made layers

Adhesive laminations

This process consists of applying an adhesive to one ply, then combining it with another before drying (wet bonding) or drying the adhesive and bonding the second ply with heat or pressure or both (dry bonding).

Wet bonding

Wet bonding is limited to laminates wherein one ply is very porous (paper) since solvent (water in this case) must be able to pass through a ply as the adhesive is being dried in heating tunnel before winding up ready made laminate. For example, foil may be laminated to a porous paper by wet bonding; but foil could not be wet laminated to another imperious film such as cellophane since the adhesive's solvent could not be released through either of two plies. Usually aqueous adhesives such as casein, sodium silicate, starches, polyvinyl acetate latex, rubber latices and resins and dextrin are employed in this technique.
Wet lamination is used most commonly to produce laminations of aluminium foil to paper/plastic films to paper or paper to paper.
Packaging materials produced this way are foil beer labels, labels for different types of glass and plastic bottles, jars and canisters, cigarette and soap wrappers, box overwraps.. Aluminium/paper laminate achieved by wet lamination constitutes a valuable substrate for further modification, for example for extrusion coating with polyethylene, very widely used laminate for dried soups and similar products.

In the schematic illustration (Fig 1) one can notice that the laminated material may be conducted through a wash or slip lacquer station where the foil is coated before it enters the drying tunnel.
This coating station is usually a graviure application system that may be used with either smooth or engraved cylinders depending on the amount of material being applied.

Dry bonding

This laminating process was born out of the specific restriction of wet bonding technique. Since two non porous materials cannot be wet bonded, a method was developed for dry bonding such materials. Solvent based adhesives are generally used in dry bonding, but water dispersions or emulsions of thermoplastics sometimes are employed too.

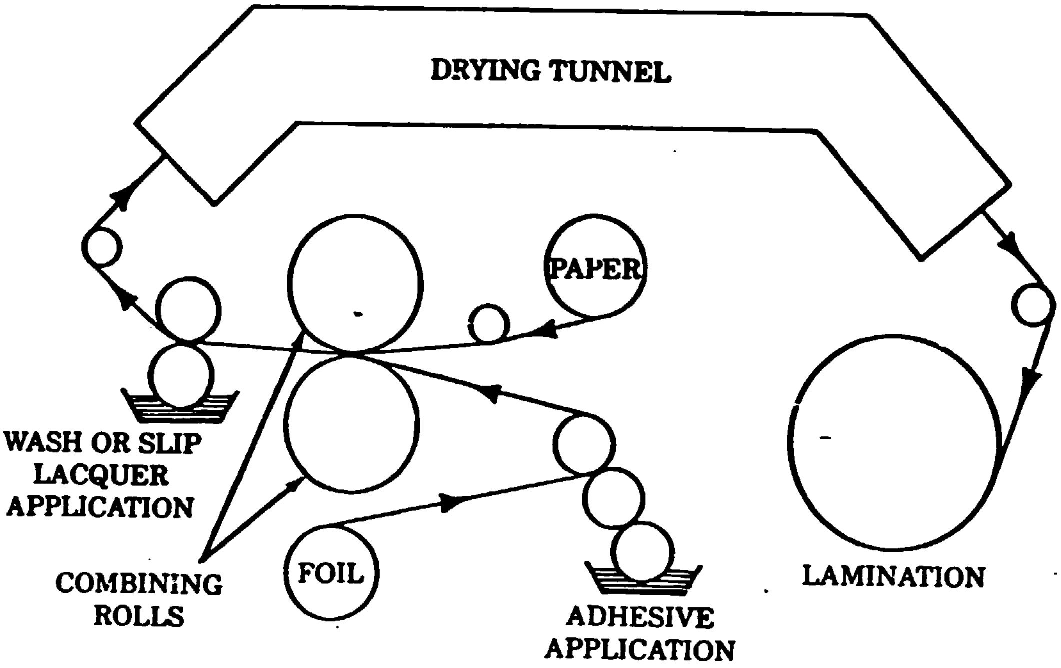


Fig I Wet bonding

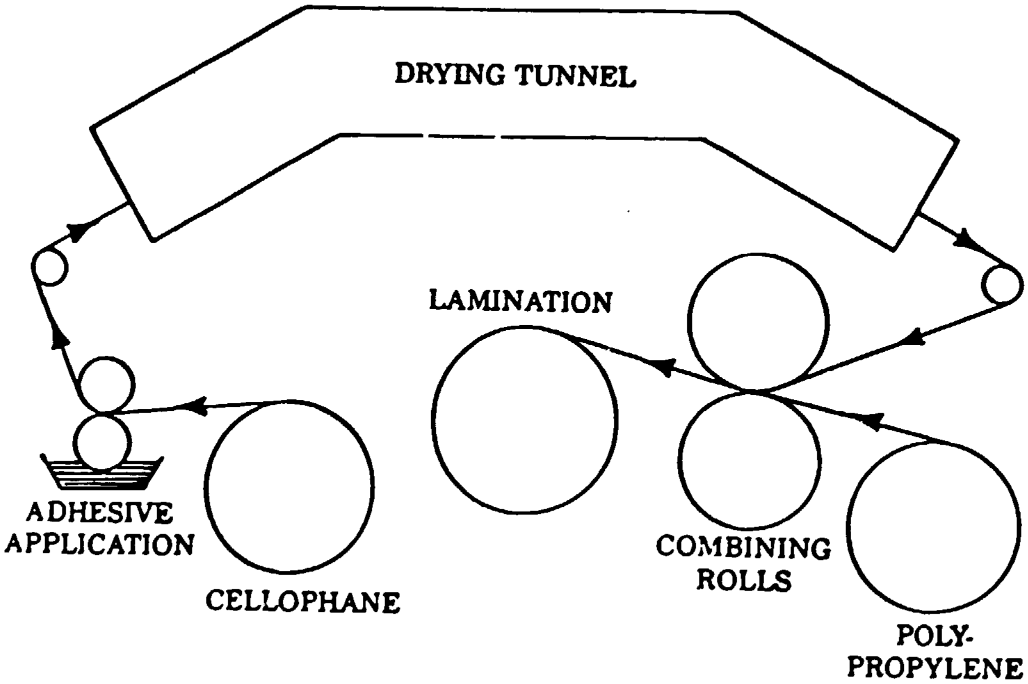


Fig 2 Dry bonding

Three types of dry bonding are commercially used today and are based on the following systems:

- curing
- pressure-sensitive bonding
- heat-reactive bonding

With curing - adhesives systems solvent-based and more rarely water-based adhesives are applied to one substrate and the solvent is removed with heat. The lamination is made to a second substrate in a combining nip and the weakly bonded lamination is wound into a roll. Full adhesive bond strength develops as the adhesive curves usually after several days at room temperature. The slow curing process develops very strong bonds.

With pressure-sensitive bonding a solvent-based tacky adhesive is applied to one substrate and the solvent is removed by drying. The dry, tacky surface is then brought together in a combining nip with the other substrate producing an instantaneous bond.

Heat-reactive dry bonding involves the use of thermo-plastic adhesives contained in a solvent solution. The adhesive is applied to one substrate and the solvent is removed as described earlier.

A second substrate is brought in contact with another one in a heated combining nip thus forming a strong instantaneous bond between the two substrates. Since the adhesive is thermoplastic, heat-reactive dry bonding is not normally used for laminations requiring high temperature resistance.

Curing type adhesives have found the widest application in production of packaging laminates, and this system will be discussed in a more detailed form.

Fig. 2 illustrates the principle of dry bonding whith solvent-based adhesives which are applied to one of the materials.

The solvent is evaporated from the adhesive, then the adhesive-coated web is combined with other materials by heat and pressure or by pressure only.

If dry bonding equipment is used to produce laminations of aluminium foil to plastic film it is desirable that it is equipped with an in-line wash or priming station as shown in Fig. 3 to prepare the foil surface for subsequent further processing, e.g. printing.

Though appearance of new lamination techniques is permanently observed on the world packaging market, dry bonding technique is still one of the most popular ones.

This is due not only to the earlier date of its first implementation but is also a result of the advantages of the technique itself. In this method a possibility exists to produce a wide range of laminantes in different combinations of bonded layers and in some cases even without exchange of the coating device and using the same adhesive.

In the case of coextrusion, lamination is usually adjusted for specific types of polymers only and deviations from the required quality of the polymers for which the line was foreseen are not tolerated.

Due to the latest development in dry bonding technique the adhesives containing as much as 80% of dry components are available. On the other hand, solventless adhesives are also in use. Up to now most frequently used are two-components-polyurethane adhesives. Polyesters and copolyesters of glycols with adipinate or isophtalic acid belong to the most popular elastomers of these adhesives. Polyisocyanite based on diphenylomethane derivate (MDI) or diisocyanite of toluilen (TDI), are usually applied as a second component. This second component is considered as a curing agent.

Contents of dry components, viscosity of the adhesive mixture, its pot life and pan life belong to basic technological features of the adhesives used in dry bonding laminations. Both components are usually supplied as a solution in ethyl acetate or methyl ethyl keton. Both components are mixed directly before lamination. Dry components content in adhesive solution used for lamination is of 25-40%, and its viscosity of 12-16 s (Ford cup dia 4 mm). Exceeding the recommended range of viscosity increases consumption of adhesive and decreases adhesion to the film carrying the adhesive. It should be remembered that water and other compounds containing OH groups are the factors that cross-link the polyisocyanite.

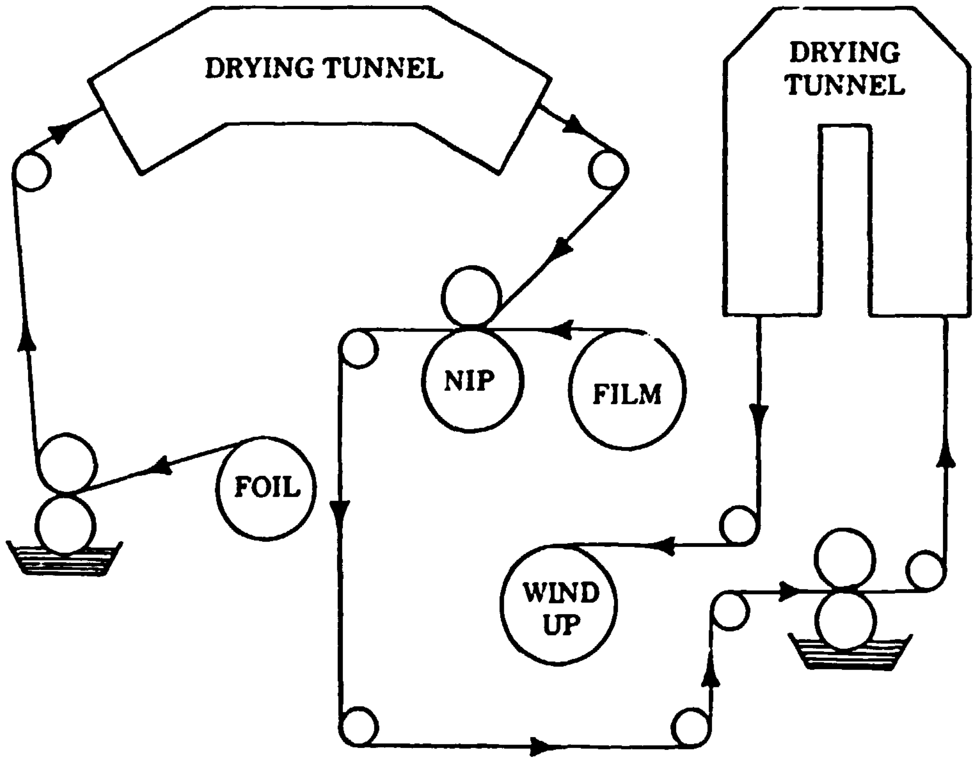


Fig 3 Priming station prior to dry bonding

For this reason the amount of water and alcohol in the solvent cannot exceed 0,3%.
Proper proportion between two components has its influence on the course of reaction of polyaddition and properties of laminates. Too high an amount of curing agent causes the britlness of adhesive layer and decreasing of laminate elasticity. If the amount of this agent is too small bond strength of laminate is often unsatisfactory.
For applying adhesive mixture one of the systemsdescribed separately is applied though the system applying engraved roll is preferable in this case.
Adhesive layer thickness (after drying) 2g/m^2 provides usually sufficient bond strength for unprinted laminates and appr. 3g/m^2 is required for sandwiched printed laminates.
The adhesive layer is usually applied on the material of higher resistance for temperature. Evaporation of solvent takes place in the tunnel usually divided into a few zones.
Heating zones are equipped with blast tubes or slots through which hot air is impinged directly onto the web of the surface.
Air blast tubes have their own exhaust provision for each zone, thus the web is not re-exposed to solvent laden air. For proper evaporation of solvents of the above indicated type the temperature of the first zones starts from 30-35 °C and is increasing from 45 up to even 70°C at the end of the tunnel in dependence of the velocity and the type of the coated film.

Gradual increase of temperature allows to avoid so called "skin" effect and provides therefore proper evaporation of solvents. After evaporation of the solvents,coated film is supplied to lamination cylinder where it is combined with another film used for lamination.
Width of the roll applying the adhesive is usually a few millimeters lower on each side than the width of the film.
The width of coated film on the other side is narrower than the other component of laminate. This protects against overflowing of the adhesive to the supporting rolls and against sealing of laminate edges.

The process of curing the adhesive begins after mixing two components of the adhesive. Due to high dilution of the adhesive the speed of reaction is very low.
The acceleration of the curing the adhesive takes place in the thin layer after evaporation of the solvents and during heating in the tunnel.
The reaction is completed, however, after some days. Up to total use of reactive groups - presence of free NCO groups can be observed by means of spectrophotometer.
Decay of NCO groups takes place usually in a period of a few days up to two weeks. In practice laminate is used for further processing (cutting) after 5-8 days and for heat sealing after 10-14 days.

In dry bonding technique the adhesive coated web is combined with a second web after maximum possible removal of the solvent in the heating tunnel. The web may be moderately warm when it emerges from the tunnel. Various adhesives demonstrate different properties as they come out of the drying tunnel.
The combining station is usually formed by two rollers. One is an internally heated steel roll with a highly polished surface. The other is a rubber covered impression roll. The steel combining roller is usually driven.
In effect the combining station also serves to draw the web through the coating and drying cycle. A speed variable device in some constructions is included in the drive train to the combining station, this provides the possibility of tension control. Pressure of the combining rollers is controlled independently on both sides.
Uniform temperature of the combining rollers is an important factor in control quality. Smoothness and clarity of laminated products may be effected by the surface smoothness of combining rollers. The tangent at which the two webs enter the combining nips is important too. Too small an angle where the webs converge may sometimes result in air pockets between two webs. It is useful for running different materials if the laminator allows for alternating the web contacts in the combining station by providing two laminated nips and making the unit-rotation reversible.

Among the films most frequently used for dry bond lamination, mutual combinations of polyolefine (polyethylene or polypropylene) films with polyamide, polyester, cellophane and aluminium foil should be mentioned.

Quality of ready made roll and geometry of the web are features of special importance in the case of lamination, and similar requirements should be fulfilled there as in the case of machine quality films discussed earlier.

Pretreatment of polyolefine films surface is required, which increases wetability of the film. This was discussed when production of PE films was analysed.
Wetability of PE or PP films during the lamination should correspond at least to the value of 38 mN/m.
This value should not exceed, however, the upper limit (45 mN/m) , to avoid a negative influence on heat sealing strength. Slip additive, required for PE films in some applications (laminates for bag making), has its influence on decreasing bond strength of laminates.
There are limitations both as far as type and amount of the slip additives used in this application is concerned.
Erucic or oleic acid are the typical slip additives used for PE films laminated by dry bonding technique and their concentration in the film acceptable in this case should not exceed 600 ppm. Higher concentration of these agents has a negative influence on bond strength of ready made laminates.
Requirements for different grades of PA films in dependence of final application of laminates were discussed, when production of PA films was analysed.

Control of the coating of adhesive amount, its overall uniformity and degree of perfection is largely dependent on the application system used. Several commonly used application systems are illustrated below.

Gravure method operating on similar principle as gravure printing is the best for controlling the solvent based coatings and adhesives generally used in flexible packaging operation.

The application cylinders used for this purpose are generally mechanically knurled steel gravure patterns. After knurling, the cylinders are chrome plated for longer wear. When lower coating weights are required, finer knurled cylinders are used along with lower viscosity coatings. When more coating weight is required, coarser screens and higher viscosity coatings are used.
In dependence of applications different gravure patterns on application cylinders are available. This is illustrated on Fig. 5 , where three types of screen patterns are given.

The screen counts indicate number of cells per linear inch. Volume of the wet coating to be applied with various screens is dependent upon the number of cells and on the individual cells' volume and their formation.

The weight of dry solids transfered to the coated substrate in dependence of screen counts for different graviure patterns and for two concentration of solids is given in the tables.

As it can be seen on the Fig 5, the gravure applicator employs a so called doctor blade which takes off the excess of adhesive and equalizes its amount in the cells.
Under the pressure of a rubber impression roll the whole amount of the coating medium is transferred from the cells to the substrate being coated.
The engraving covers the entire width of the cylinder; therefore the rubber impression roller must be cut back to the width of the web being coated. Greater (appr. 5 mm on each side) width of the web comparing with the impression roll protects against overflowing the adhesive or other coating medium on the edges of the web, which are practically not coated.

Gravure system gives most uniform and reproducable coating weight and provides the possibility of using it with a variety of solvent systems (no rubber or composition rollers are in contact with the coating medium).
It should be mentioned, however, that usually one gravure cylinder is applied for always the same substance of the coating weight and only small changes are possible by concentration changes of the coating solution.

Squeeze roll system (Fig. 6) may be used for application of low to medium viscosity solvent based coatings, water based dispersion or low viscosity wax hot melts

ROTOGRAVURE

- Best for application of low to medium viscosity solvent based coatings, adhesives or primers.
- Gives most uniform and reproducable coating weight.
- Wide variety of solvent systems may be used since no rubber or composition rollers are in contact with the coating material.
- May be internally heated for application of hot lacquers or low viscosity hot melts.
- May use auxiliary smoothing roll to assist in flow-out.
- May be used for pattern applications of coatings.
- Peripheral speed of the knurled or engraved roller must be synchronized with web speed.
- Change in web width requires undercut rubber impression roller.

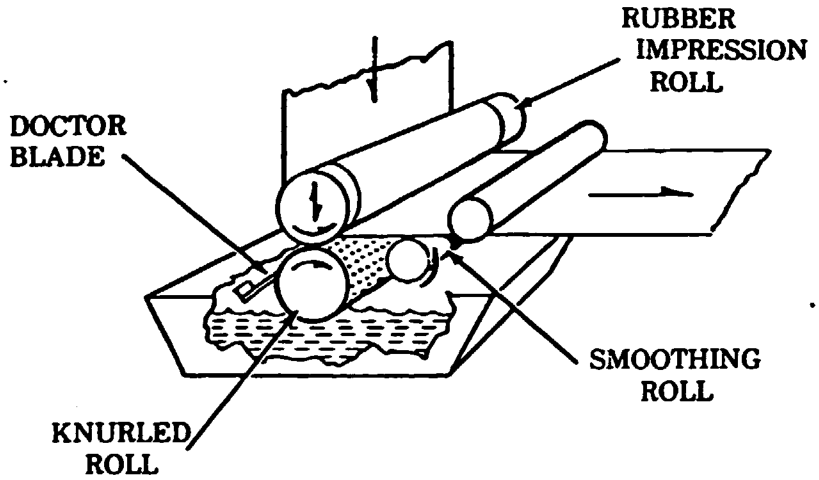
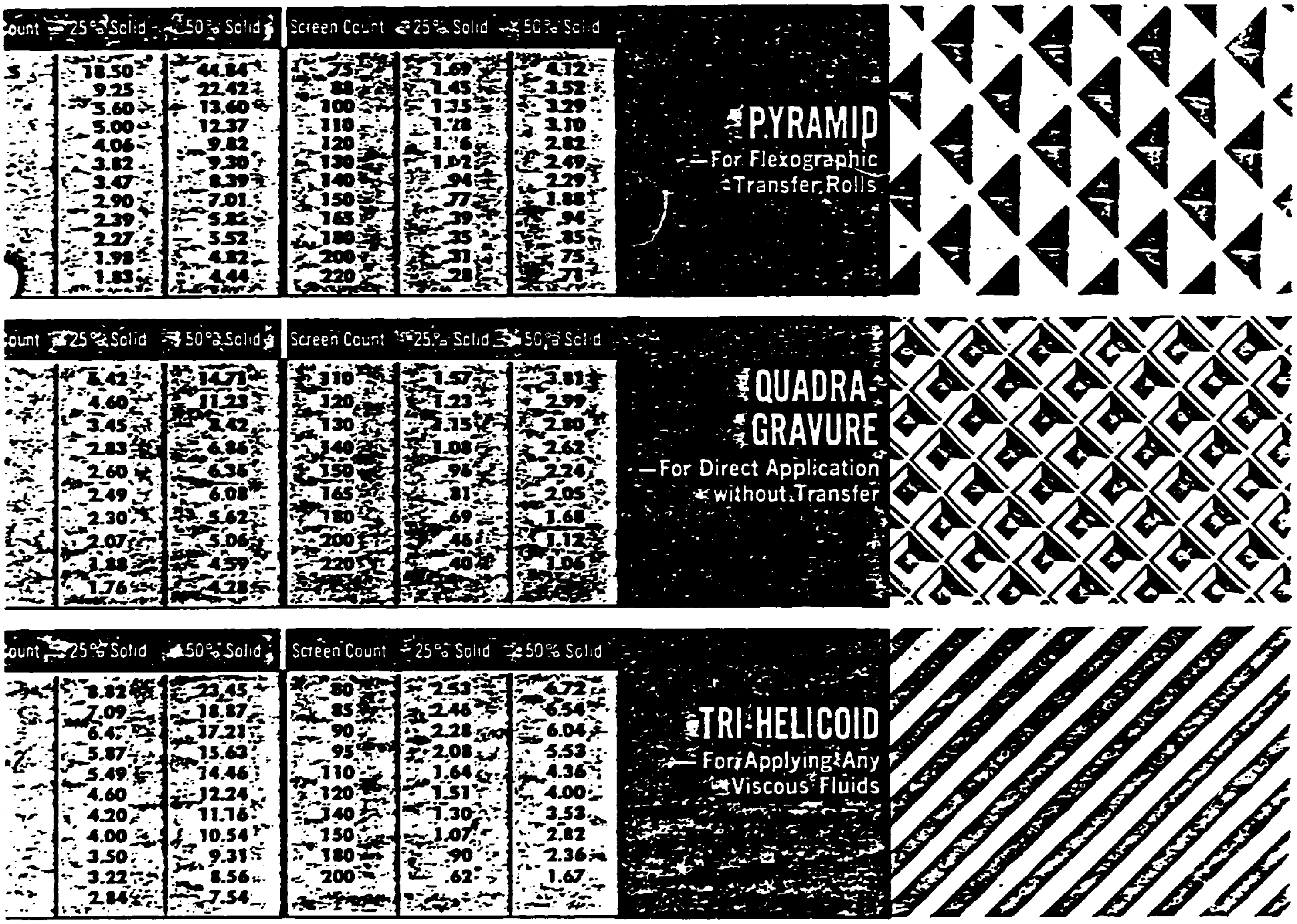


Fig 4 Graviure adhesives applicator



ount	25% Solid	50% Solid
5	18.50	44.84
	9.25	22.42
	3.60	13.60
	5.00	12.37
	4.06	9.82
	3.82	9.30
	3.47	8.39
	2.90	7.01
	2.39	5.82
	2.27	5.52
	1.98	4.82
	1.83	4.44

Screen Count	25% Solid	50% Solid
75	1.69	4.12
88	1.45	3.52
100	1.35	3.29
110	1.28	3.10
120	1.16	2.82
130	1.02	2.49
140	.94	2.29
150	.77	1.88
165	.39	.94
180	.35	.85
200	.31	.75
220	.28	.71

PYRAMID

—For Flexographic Transfer Rolls

ount	25% Solid	50% Solid
	3.42	14.71
	4.60	11.23
	3.45	8.42
	2.83	6.86
	2.60	6.36
	2.49	6.08
	2.30	5.62
	2.07	5.06
	1.88	4.59
	1.76	4.28

Screen Count	25% Solid	50% Solid
110	1.57	3.81
120	1.23	2.99
130	1.15	2.80
140	1.08	2.62
150	.96	2.24
165	.81	2.05
180	.69	1.68
200	.46	1.12
220	.40	1.06

QUADRA-GRAVURE

—For Direct Application without Transfer

ount	25% Solid	50% Solid
	8.82	23.45
	7.09	18.87
	6.47	17.21
	5.87	15.63
	5.49	14.46
	4.60	12.24
	4.20	11.16
	4.00	10.54
	3.50	9.31
	3.22	8.56
	2.84	7.54

Screen Count	25% Solid	50% Solid
80	2.53	6.72
85	2.46	6.54
90	2.28	6.04
95	2.08	5.53
110	1.64	4.36
120	1.51	4.00
140	1.30	3.53
150	1.07	2.82
180	.90	2.36
200	.62	1.67

TRI-HELICOID

—For Applying Any Viscous Fluids

Fig 5 Different screen patterns for gravure applicator

SQUEEZE ROLL

- May be used for application of low to medium viscosity solvent based coatings, water based dispersion, or low viscosity wax hot melts.
- System must avoid use of solvents that will affect rubber or composition application rollers.
- Extremely difficult to control or reproduce exact coating weights.
- Frequent web width changes will cause web edge marring of application or squeeze roll.
- Generally used in coating weights up to 2.0 lbs. per ream (4.0 g/sq. m).
- Three high system provides for use of slightly higher viscosities or control of coating weight in low ranges.
- Three high system provides a reverse roll coating option.

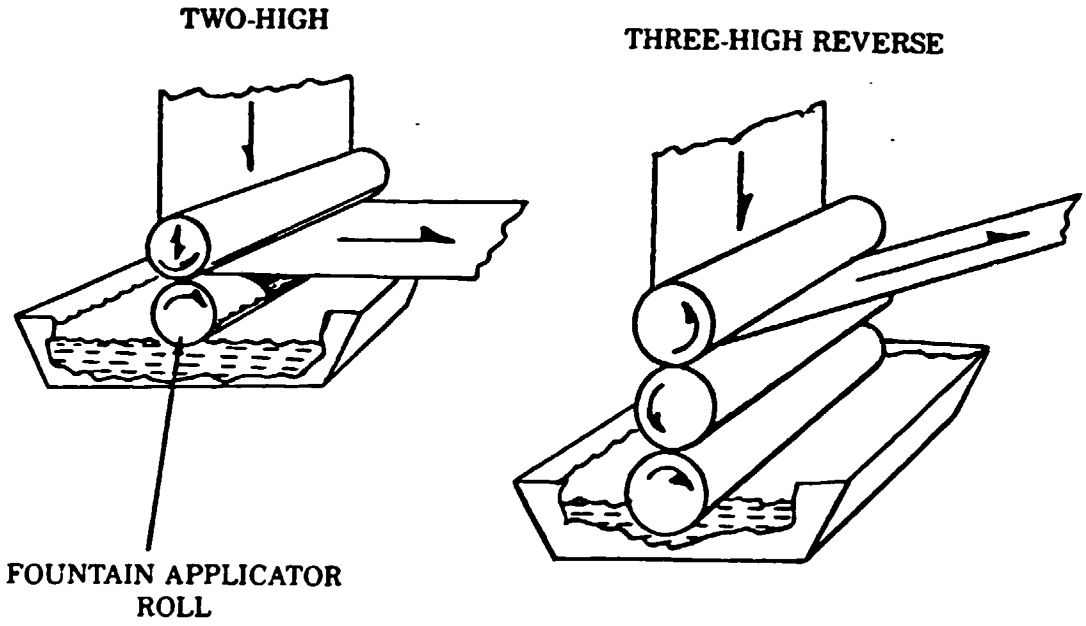


Fig 6 Squeeze roll applicator

This system must avoid use of solvents that will affect the rubber of the composition application rollers. It is extremely difficult to control or reproduce the exact coating weights and it is generally used for coating weights up to 4 g/m^2.

The Three-high system (reverse roll coating option) allows the use of high viscosities or control coating weight in low ranges. The Tension Kiss system (Figure 7) may be used for application of low viscosity solvent or water-based coatings on metal foils, non extensible films or high tensile strenght papers. This system is very simple in situations requiring frequent web width changes for non critical applications at low speeds. The coating weight is extremely difficult to control because of variations in tension, speed, coating viscosity and substrate flatness.

The Wire Wound Rod (Mayer Bar) system (Figure 8) may be used for application of low viscosity solvents-based coatings, water dispersion or latices, hot waces or plastisols, at low speeds. The diameter of the wire wound on the rod determines the thickness of the coating. The extreme ease of changing the bar wire size provides for wide latitude in coating weight metering. The system is not suitable for light gauge extensible films, low tensile strenght papers or easily abraded substrates. Mayer rods can cause scratching. Uniformity of coating is highly dependent on uniform tension and flatness of web.

The Air Knife system (Figure 9) is the best one for application of water-based latices (PVDC type, for example) on paper and paper board and is generally effective in controlling coating weights in the wide range from 4 to 30 g/m^2. In this system the excess of the dispersion is taking off the web by use of a so-called air knife, so called because of the stream of air blown under the pressure from the slot. The system is easily adaptable to changes in the web width, but is highly dependent on density, viscosity, surface tension of coatings and the uniformity of the substrate surface.

Wax lamination

As the name implies, wax lamination technique uses wax or resin-modified wax as so-called hot melts containing for example ethylene vinyl acetate copolymers, low molecular weight polyethylene or other resins.

The melted wax is applied to one of the materials to be laminated, whereupon it is brought into contact with the second web under moderate pressure. The material is then chilled, causing the wax to freeze and bond the two plies together. The equipment (illustrated in Fig. 10) is widely used to produce foil-paper laminations that will subsequently be printed. A foil treating station and a drying tunnel may be put between stations E and F. Normally light weight and/or porous papers are used, the wax is applied to the paper ply as illustrated. 50 to 53° paraffine wax may be used to laminate foil and paper where only superficial bond strength is required. Highly refined microcrystalline waxes of approximately 53° C melting point are common laminates for wax bonded foil-paper, paper-paper and cellophane-cellophane combinations. Variations in bond strength, pliability, water and grease resistance and moisture vapour impermeability properties are achieved by manipulation of the amount of wax adhesive applied between 8 up to 50 g/m^2, and/or by modifying the wax with up to 10% of proper resin. All wax or resin modified wax laminations are characterized by a "peelable bond" of low or moderate strength. A comparison of bond strength of different types of laminates can be seen in tables 6 and 7.

Lamination of Al foil with parchment paper widely used for butter and margarine packing on overwrapping machines is a typical application of the described type of materials. Mutual combinations of different grades of cellophane with Al foil are also common in Great Britain for example.

TENSION KISS

- May be used for application of low viscosity solvent based or water based coatings on metal foils. non-extensible films or high tensile strength papers.
- Coating weight extremely difficult to control because of variations in tension, speed, coating viscosity and substrate flatness.
- Not recommended for high speed operations.
- Extremely simple in situations requiring frequent web width changes for non-critical application of low viscosity materials at low speeds.

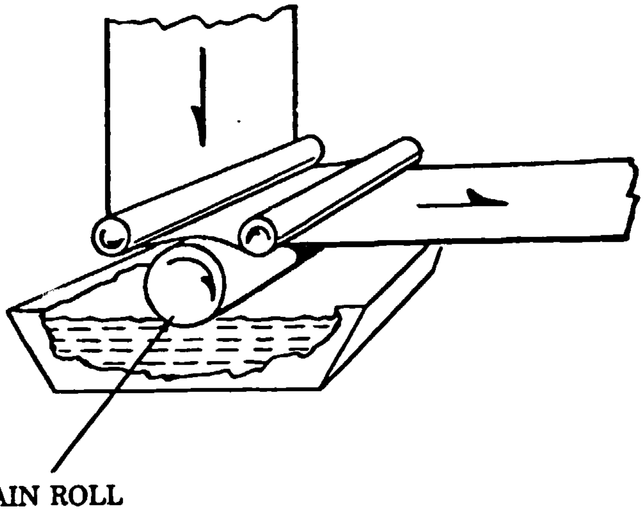


Fig 7 Tension kiss applicator

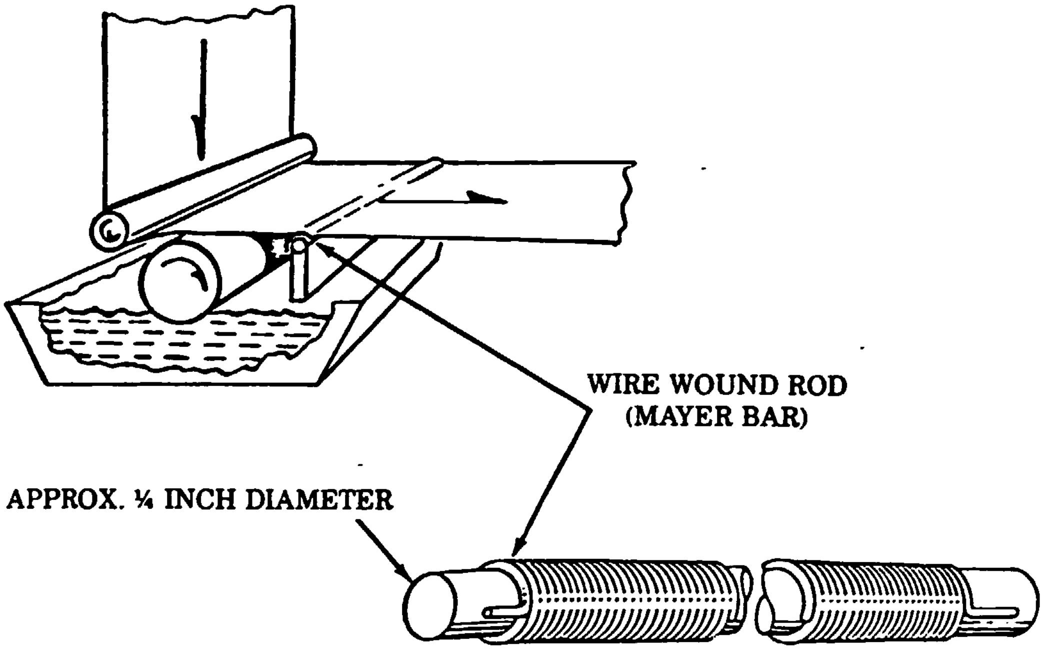


Fig 8 Applicator with Mayer bar

AIR KNIFE

- Best for application of water based latices on paper and paperboard.
- Highly dependent on control of density, viscosity, surface tension of coatings and on the uniformity of the substrate surface.
- Easily adaptable to changes in web width.
- Contributes to foaming of some latex materials.
- Generally effective in controlling coating weights in the 2.0 to 15 lbs./ream range.

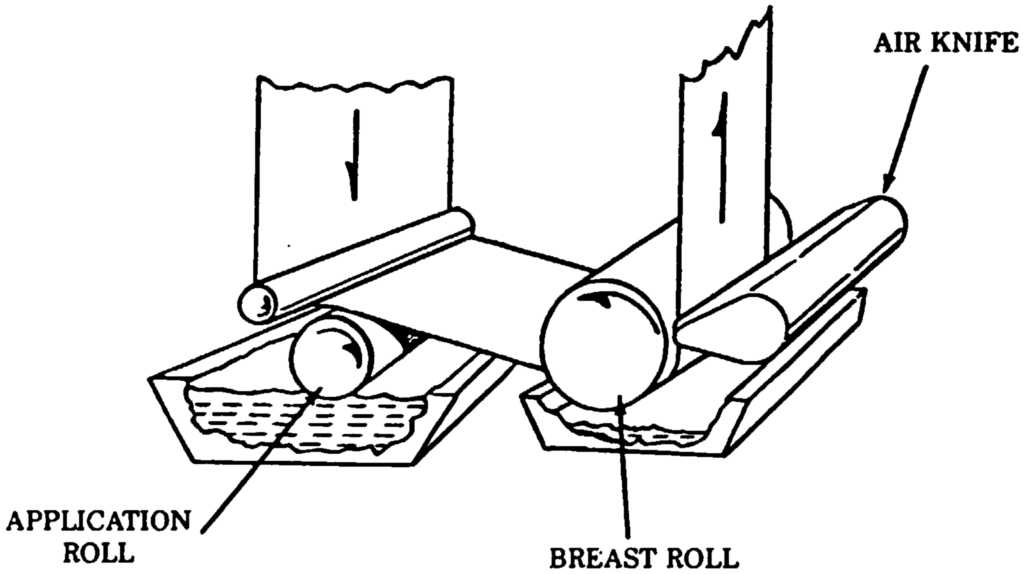


Fig 9 Applicator with air knife

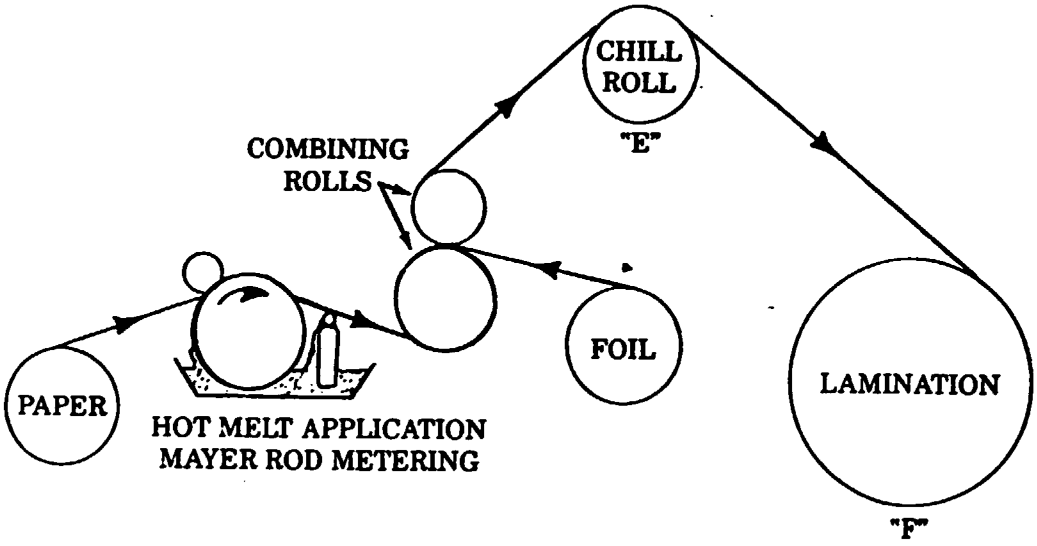


Fig IO Hot melt and wax lamination

Laminates produced by extrusion coating and lamination

This system of producing the laminates was previously used for combining paper with plastic (mainly low density polyethylene). Nowadays extrusion coating or laminating is one of the techniques widely applied for production of different combinations of plastics and combinations of plastics with traditional materials (cellophane, paper and aluminium foil).

The previously described laminates can also be produced by the extrusion technique, and the properties of laminates produced by extrusion coating, for example of PA/PE laminates, do not differ from those produced by dry bonding.

Low density polyethylene is still the most popular substance used in the production of laminates by coating and laminating, though some others find some applications too, as illustrated in Table 1. The choice of either of the lamination techniques on a production scale depends to a great extent on the production programme.

The extrusion technique is more frequently applied when the same type of laminate is produced on a larger scale and frequent changes in the production programme are not expected. The stoppage of the extrusion line and return to movement may involve overheating of the polymer and may cause the necessity of a time-consuming cleaning of the head before putting the line in operation again. It should also be mentioned that in recent times coextrusion coatings are being developed as a means to reduce costs in packaging areas, where heavy gauges of expensive resins are needed, coextrusion coatings combining low cost resins with high cost resins are being used. An example for this would be a low density polyethylene/ionomer coextrusion to replace an equal gauge of ionomer. Generally speaking in both extrusion and coextrusion coating and laminating it is possible to achieve thinner layers, even as thin as 5 mm.

Dry bonding technique allows for greater flexibility of the production programme and change from one type of laminate to another does not involve any problems.

The discussed techniques have advantages and disadvantages, but one should not expect extrusion techniques to always eliminate solvent retention problems, because these techniques often require the use of so-called primers used for increasing adhesion of the extruded layers to base materials. These primers are usually applied in organic solvents.

It should be mentioned, however, that in the case of coextrusion there is no need to use solvent type primers which are replaced by the use of additional proper type polymer layers like ionomer for example, which involves an increase of the adhesion between resins not adhering to each other like PE and PA for example.

In the case of dry bonding technique thinner layers than 30 mm are very rarely used.

Theoretically there is no reason why any plastic which is normally processed by extrusion techniques should not be coated on paper or other substrates. The most common extrusion coating resin used is low density polyethylene. Extrusion and coextrusion with ionomers, polypropylene, some types of copolymers as ethylene methyl acrylate and ethylene vinyl acetate are also common. Some examples of extrusion coated papers are presented in Table 2.

Extrusion coating with polyethylene has several advantages over adhering a prefabricated polyethylene film to paper. First, thin films of polyethylene are difficult to handle and to maintain flat; handling them requires very low tensions which are difficult to control at high speeds. Secondly, extrusion coating temperatures are sufficiently high, so that good mechanical bonds are obtained by resin penetration into the porous paper substrate.

For achieving the same adhesion level in the case of lamination with prefabricated film laminated to paper the use of proper adhesive is necessary. This involves an extra cost in comparison with the extrusion technique.

The principle of extrusion coating is illustrated in Fig. 11.

In this operation the substrate may be directly primed before coating or corona treated before coating. Various substrates require different combinations of pretreatment to achieve the desired levels of adhesion. The most important variables in this process are:

- resin composition
- operating conditions
- substrate pretreatment.

TABLE I

COMMON COATING MATERIALS USED IN COMPOSITE STRUCTURES

Material	Primary function	Common method of application
Ethylene vinyl acetate copolymer	Heat sealibility	Extrusion, solvent
Polyvinylidene dichloride	Moisture, oxygen grease barrier	Solvent, aqueous
Ionomer	Grease resistance heat sealibility	Extrusion, solvent
Paraffin waxes	Low temperature heat sealibility, moisture and oxygen barrier	Molten solvent
Cellulose nitrate	Machinability grease resistance heat sealability	Solvent, aqueous
Alkyd Amines	Gloss, thermal resistance	Solvent
Silicones	Slip, release	Solvent
Polyester urethanes	Gloss, thermal resistance	Solvent
Low density polyethylenes	Heat sealability	Extrusion
Polypropylene	High temperature heat sealability	Extrusion
Ethylene acrylic acid	Grease resistance heat sealability	Extrusion solvent

TABLE 2: Extrusion Coated Papers

Substrate	Coating	Thickness (Mils)	Comments
milk carton stock	polyethylene dens .92	.2	Milk carton board replacing wax coatings. No flaking tendencies, speeds up to 3,000 fpm.
20 pound pouch paper	polyethylene dens .92	.5-2.0	For heat sealable pouches having good moisture barrier and strong heat seals.
20 pound pouch paper	polyethylene dens .96	.5-2.0	Greater stiffness, better high temperature properties, better barrier than lower density polyethylene.
40 pound Kraft	polypropylene dens .90	.5 mils and up	Better greasem moisture, and heat resistance than comparable thicknesses of polyethylene.
40 pound Kraft	nylon dens 1.16	.5 mils and up	Gives exceptional toughness, tear and abrasion resistance - very good grease and oil barrier but relatively poor water barrier.

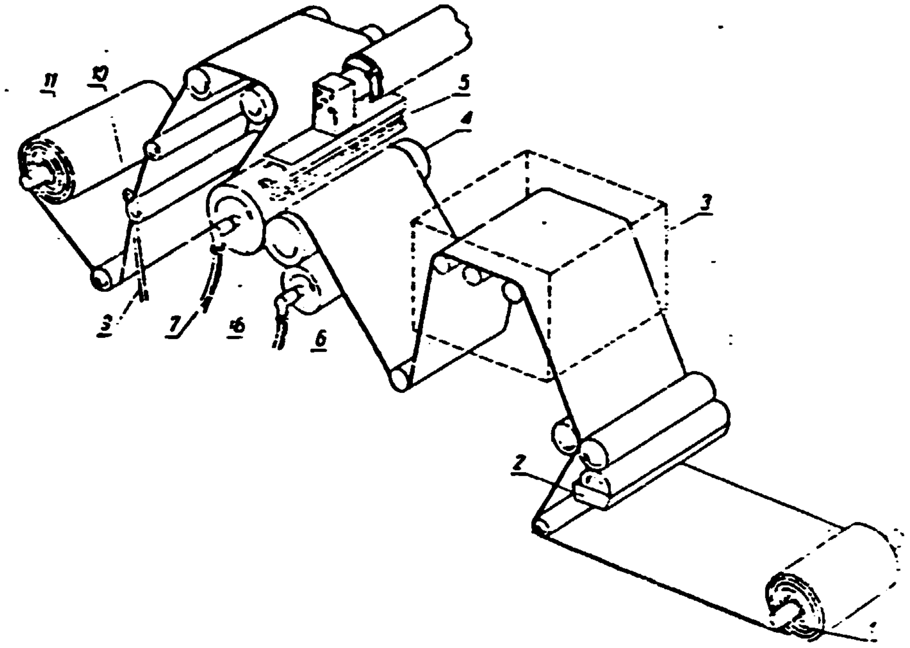


FIGURE 11

Principle of laminates making by coating with polyethylene.

1. Coated film,
2. Applying the primer
3. Dryer
4. Pressing roll
5. Flat die
6. Cooling system
7. Cold water inlet
8. Chilled roll
9. Cutting the edges of the laminate
10. Cutting nife
11. Rewinding of the laminate.

The generally most used LDPE may be deposited on the substrate in the range of thicknesses of 0.005 to 0,075 mm, but practically coatings thinner than 10 µm and thicker than 50 µm are very rarely in use.

The thickness of the coating can be varied through changing the linear take-off speed from the die and through changing the extrusion rate. Slot die opening (flat die extrusion system) should not be less than 0.5 mm. LDPE is extruded at a temperature of 232-343°C. Extrusion coating requires resins of higher MFI, usually in the range of 5 to 15 g/10 min. Lower molecular weight PE (higher MFI) is more suitable for high speed coating. Resins of higher molecular weight (lower MFI) are preferable for producing thicker coatings at lower line speeds. Extrusion temperature and the distance from the slot of the die to the chill roll belong to the major operating conditions. With a temperature increase the adhesion is improved. This is a result of higher oxidation of the polymer streat leaving the die. On the other hand lower viscosity at higher temperatures promote better surface wetting of the substrate. It should be noted, however, that the higher the temperature the greater is the probability that the odour may remain in ready made material. The increase of the degree of oxidation may involve a decrease of heat sealing strength. It was proved experimentally that at an extrusion temperature of 218 to 260°C no odours are developed in ready made material. At this temperature, however, adhesion may occur to be unsufficient, and in this case imrpvement of the adhesion can be achieved by the use of primers or surface pretreatment.

If very high temperature has to be used (for example 330°C) odour development can be kept to a minimum by flooding the space between the die and nip roll with neutral gas (N_2; CO_2). This simply prevents oxidation of polymer. In some cases only one side of the film is flooded with neutral gas. In this case adhesion is promoted on one side without affecting heat sealability and development of odours on the other side.

Following phenomena are taking place when hot film is leaving the die and entering the nip roll:

- decrease of its thickness even as much as 60 : 1
- cooling
- oxidizing

For better adhesion shorter distance between the nip roll and the die is required, what results in higher temperature at the nip roll. In some cases aluminium reflectors protecting hot film are used what provides higher extrusion temperature.
Increasing draw down ratio involving decrease of thickness may lead to poorer adhesion.
For example with increase of the speed from 60 to 120 m/min involving decrease in thickness from 0,025 to 0,012 mm the adhesion can drop from useful 200 cN/25mm to unpractical near to zero cN/25 mm.
It is understandable that the shorter the time of contact of the hot film with the air, the lower the oxidation; the faster the cooling of thinner film at the nip roll, the lower penetration to the substrate.

Following figures illustrate the comparison of barrier properties of different polyolefine resins coatings (0,025 mm thickness).

	oxygen permeability $cm^3/m^2 \cdot 24h/0,1MPa$	water vapour permeability $g/m^2 \cdot 24h$
LDPE	9500	1,1
HDPE	4200	0,7
PP	3700	0,6

Comparing polypropylene as a substance for extrusion coating with previously discussed polymer following statements can be made:

Pinholes free coatings are produced at thicker polymer layers starting from 25 µm Extrusion lines consist of extruders of L/D ratio from 28:1 up to 32:1.
Compression ratio 3,5 to 4:1 is typical in this case.
The dies of the same design as for processing of PE are used, die opening however is usually narrower. Higher output rate provides smaller variation in the coating thickness.
PP cannot be oxidyzed by proper increase of the temperature as it was possible in the case of polyethylene, because of an extremely low viscosity of PP in melted form.
The increase of bond strength can be provided by minimizing the possibility of cooling the flowing stream of polymer prior to its contact with the substrate.
For increasing bond strength liquid primers can be used but preheating of the substrate is sometimes sufficient.

Influence of substrate on the adhesion of extruded layer

As substrates for extrusion coating porous materials - different types of paper (kraft, pouche paper), milk carton and board -, as well as non-porous materials - cellophane, aluminium foil and plastic films (e.g. polyester, polyamides) are used.

When porous substrates are used for coating, adhesion is developed by mechanical interpenetration of polymer into the paper fibers. In this case it happens that no pre-treatment of the substrate is required.

However, even in the case of paper coating, specially when production at high speed is required surface pretreatment may prove to be usefull. Paper coating extrusion lines nowadays usually employ a corona treatment assembly.

For nonporous substrate as aluminium or plastic films as a rule surface treatment is required.
Following types of surface treatment are in use:

- corona treatment
- primer application
- combination of both

Previously used flame treatment though still used for bottles is without practical meaning in the case of the film. The principle of corona treatment was explained when production of LDPE film was discussed.
The effect of corona treatment on the adhesion of different types of substrate is illustrated below.

It should be mentioned that slip additives influence the effectiveness of corona treatment.
These types of substrates which migrate easily on the surface of the film constitute the obstacles for achieving the required level of surface pretreatment and influence negatively the adhesion of extruded layer.

Primer treatment of substrates

A number of substances have been found to be effective in promoting polyethylene adhesion to a variety of substrates. They are used in a very thin layer (parts of gram/m^2).
Due to the chemical nature of these substances oxidized extruded polyethylene adhere strongly to them. These substances on the other hand are able to adhere very strongly to the substrate itself.

Optimum concentration and the thickness of the primer layer has to be found experimentally.

Following types of primers have found commercial utility:

- polyalkyleneimine (polyethyleneimine)
- organic titanates
- polyurethanes
- polyesters
- colloidal silica

The following tables show the effect of primers used for improving adhesion of extruded polyethylene on polyester and aluminium films (Tables 3 and 4).

General improvement of adhesion of PE layer to the substrate involved by primers is evident. A different behaviour of the same primer used for different substrates can be observed. In the case of polyester film higher effectiveness of the primers was observed in the case of thicker coating (higher combining temperature).

Aging may improve or degrade the bond strength of a primer and aging test is extremely important for evaluation of the primer.
In the case of Al foil, primers appeared particularly effective in promoting adhesion of thin coatings (low combining temperatures) but only showed marginal improvements in the adhesion of thicker coatings (thicker coatings adhere well to untreated aluminium).

The effectiveness of polyethyleneimine primers can be improved on certain substrates by formulating these primers with oxidizing agents (like CrO_3 for example).
These agents cause polyethylene to adhere at lower temperatures or higher speeds due to interface oxidation which enables materials to be better bonded by the imine primer.

As it was explained before an increase of extrusion temperature involves (due to excess oxidation) a decrease of heat sealing strength.

The possibility of providing sufficient adhesion at a lower temperature ensures at the same time an increase of heat sealing strength.

Extrusion and coextrusion lamination

Extrusion lamination can be considered as a specialized application of extrusion coating.
In this technique extruder equipped with slot die is used to melt and continuously apply a controlled amount of very

viscous melted resin, usually polyethylene, sometimes ionomer, or both types of these resins simultaneously (in the case of coextrusion) directly between the two web materials being laminated. The bond is achieved as the melted resin resolidifies.

Extrusion laminating is the most frequently used technique for combinations such as foil/polyethylene/paper, cellophane/polyethylene/foil, paper/polyethylene/paper, polyester/polyethylene/foil and cellophane/polyethylene/cellophane.
The following figure illustrates schematically extrusion laminating in its most basic form (Fig. 12).

The next figure presents an extrusion lamination line that has been equipped with all necessary priming and coating stations. (Fig. 13)
Many commercial establishments are similarly equipped.

As it was explained before polyethylene does not have a natural and adequate adhesion to all substrates. Similarly as in the case of extrusion coating primers or precoating calculated to augment the bond or in some cases to improve resistance to chemical attack are applied to either the foil, the film or the paper being laminated.
It is desirable both technically and economically to apply such coatings in line. Since many of the foil/paper laminations that are extrusion laminated or subsequently printed or coated, it is advisable to add an in-line or priming unit after laminating.

Coextrusion lamination was introduced as a means of improving adhesion between the bonded layers.
The use of ionomer in this case increases adhesion to many substrates to such a degree that there is no need to use additional primers. The principle of the coextrusion lamination process is illustrated in Fig. 14.

Properties of the laminates

Barrier properties and mechanical strength of the laminates mainly depend on the type of the resin used in the production and the thicknesses of the proper plies. The influence of the production method is not very high in this respect.
There exists, however, a group of features mainly dependent on the production method and conduction of the technological process. Bond strength, solvents retention, presence of odours, quality of ready made roll, slip characteristic adjusted for thermoforming can be mentioned here.

Because of an enormous variety of laminates available on the market their properties will be described on the basis of some types of laminates only.

Table 3 Adhesion Strength Data - Polyethylene on PETP Film

Type of primer	Extrusion coating thickness nm	Bonding Strength g/inch	
		Fresh	After IO days
none	25	0	0
	I2,5	0	0
polyethylene imine	25	568	844
	I2,5	283	468
polydibutyl titanate	25	289	504
	I2,5	I53	325
colloidal silica	25	372	0
	I2,5	459	68

Table 4 Adhesion Strength Data - Polyethylene on Aluminium Foil

Primer	Extrusion coating thickness nm	Adhesion Strength	
		Fresh	After IO days
none	25	2I2	459
	I2,5	0	45
polyethylene imine	25	3I3	295
	I2,5	268	28I
polydibutyl titanate	25	450	699
	I2,5	256	404
colloidal silica	25	535	547
	I2,5	262	243

Fig I2 Extrusion laminating

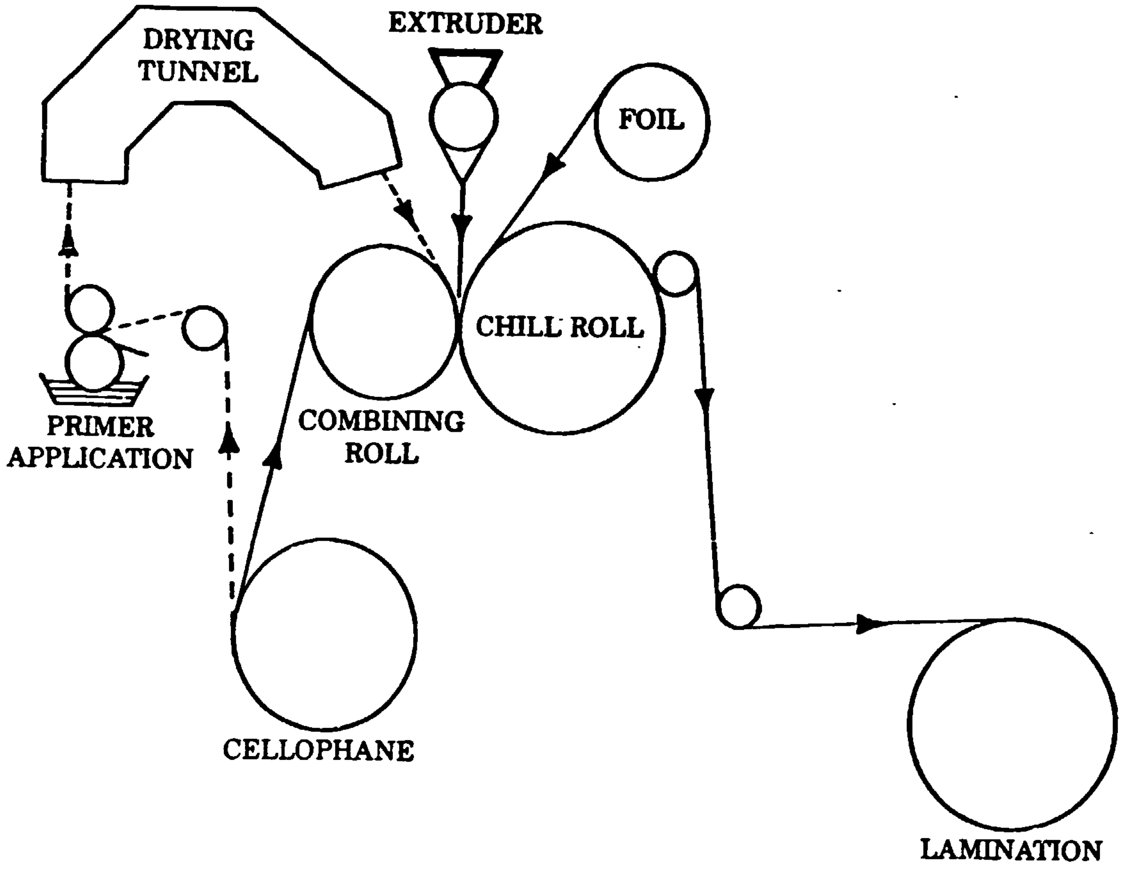
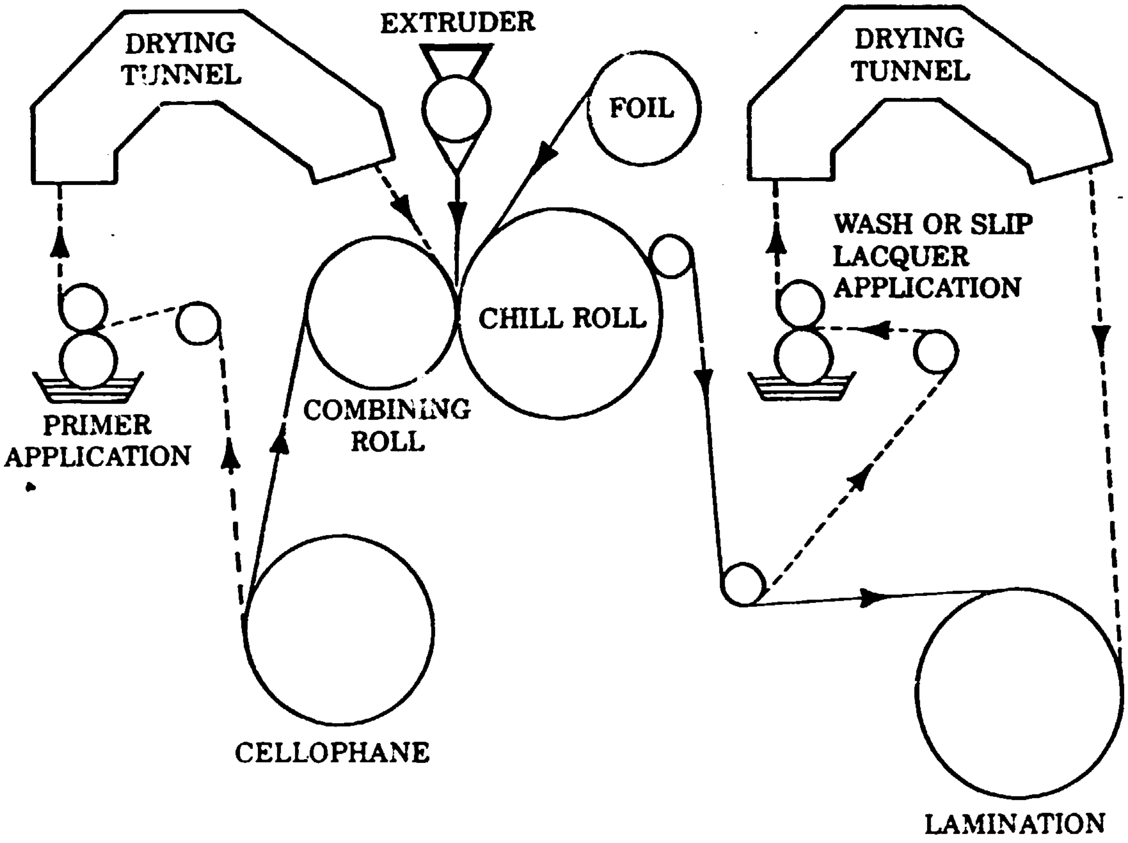


Fig 13 extrusion laminating line combined with priming station and lacquer coating one side of laminates.



Different combinations of PA, PE and PP made by the dry bonding technique have been chosen as an example.

Properties of the films before lamination are given in Table 2 presented in the chapter dealing with polyamide films. In the next table, properties of laminates made with the use of these films are shown (Table 5).

The properties described in the table are mainly a result of the type of polymers used for their production. Properties which are influenced by the process itself are included in the specifications given separately for ready made laminates and for films used in their production.

The influence of the thickness on tensile properties is not especially significant. The influence of the thickness on tear strength of PA films is relatively higher. The strength of PETP/PE laminates is lower, when comparing with PA/PE laminates. Water vapour permeability is practically on the same level for all presented laminates.

Permeability of gases decreases with the increase of PA film thickness.

Constant permeability of PETP/PE laminates independently of humidity of the gases and increase of this permeability for laminates containing PA films should be underlined.

As it was indicated before, some PA/PE laminates are predestined for deep drawing. In this case 2- 2,5 times reduction of preliminary thickness, causing the increase of gas permeability can be expected. This increase is not so high however, because films orientation taking place at the same time involves a certain increase of the permeability coefficient.

Resistance to oils and greases of all described laminates is very good and is the result of lack of pinholes and good resistance of the products of PA and PETP films and acceptable tightness in the case of PE films, remaining in direct contact with the above mentioned products.

Due to the specific properties of polyester films PETP/PE laminates create an especially good barrier against transmission of odours. Generally speaking, polyester layer in the case of PETP/PE laminates and PA for PA/PE laminates, decide of the value of permeability for gases (excluding water vapour permeability) of both types of laminates.

Low resistance of PE in a higher temperature makes it impossible to sterilize product packed in PA/PE and PETP/PE laminates.

Properties of the laminates with participation of PETP or PA films being a result of the nature of the films used for bonding

TABLE 5

Property	Unit	Testing method	Type of laminates					
			PETP/PE		PA/PE			PA/PP
			I2/70	20/70	30/70	40/70	50/70	30/70
Thickness	nm	PN 75/C 89090	82	90	I00	II0	I20	I00
Substance	g/m^2	PN 64/P 50I29	83	88	I00	III	I22	I00
Yield	m^2/kg	-	I2	II	I0	9	8	I0
Tensile	N/I5mm	PN-70/C-089092						
MD			40	40	50	60	65	50
TD			50	35	40	50	55	40
Elongation	%	PN-70/C-89092						
MD			I00	330	4I0	490	380	420
TD			200	370	440	5I0	450	450
Stiffness	N/m	PN-74/C-79II9	I3	I2	I6	I7	I8	I7
Tearing resistance								
MD	N	PN-65/P-50I3I	0.5	I,I	I,4	2,2	2,3	I,5
TD			0,7	2,I	2,5	3,2	3,7	2,6
Coefficient of the friction PE PE with slip additives		PN-72/-079II8	$< 0,4$					
without " "			$> 0,4$					
water vapour permeability 38°C 90%r.h.	g/m^2d	PN-72/0-79III		3,2	-	4,0		
Gas permeability	$cm^3/m^2.d$							
20°C 0% r.h. O_2		PN-72/0-79117	70	20	I5	I0	5	I0
75% r.h.			60	50	30	20	I0	25
0% r.h.			230	55	40	25	I0	35
CO_2 75% r.h.			220	I40	I00	70	40	I00
Resistance for oil and grease			non permeable, inter layer indicates some swelling under longer exposition					excellent
Application temperature			- 50 to + 90° C *					- I0°C to +I35°C

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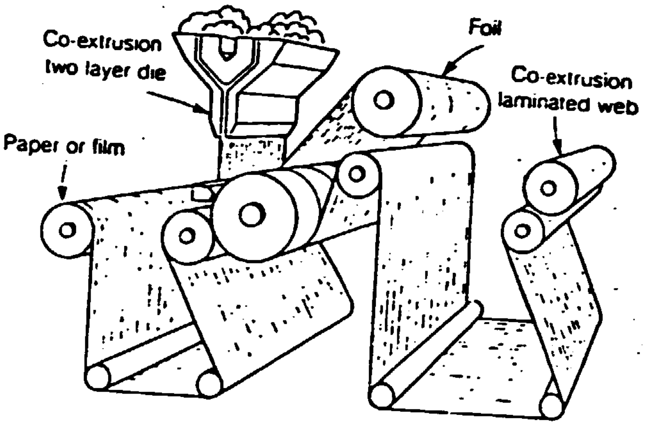
* in the case of small amount of the air inside possible heating at I00°C or up I05° in the case of applying contra pressure.

FIGURE 14
CO-EXTRUSION LAMINATION PROCESS



In some cases only when the amount of air inside the package is relatively small and contra-pressure is provided, products packed in these laminates can be heated up to 105°C.

PA/PP laminates on the other hand are the examples of materials adjusted for heat sterilisation of the products, and an increase of temperature up to 135°C is acceptable.

All types of laminates described in the table are suitable for vacuum and neutral gas packages. PETP/PE and PA/PE laminates consisting of lower thicknesses of PA films are used in pouches form or as a cover of thermoformed packages, where, on the other hand, thicker PA films starting from 30 µm are applied.

Products such as ham, bacon, sausages (including the hot-dogs type), frozen fish, smoked and processed fish, cheese are packed in pieces or in sliced form with the use of the above described laminates.

Bond strength of ready made laminates depends mainly on the type of combining substrates, the pretreatment system, the type of the agent used and conditions of the process. Results achieved by my institute (interlaboratories studies made in co-operation with Czechoslovakian institute - IMADOS are presented in Tables 6 and 7.
They contain the results for different types of laminates available in both countries. Two different methods are applied in these studies. High differences in dependence on type of laminate can be observed. Not in each case there exists a need to use the laminate with very high bond strength. In some applications even as low a bond strength as was found for Extrasvit is fully acceptable. In other cases (e.g. thermoforming of PA/PE laminates) quite a high bond strength is required for protecting the laminate against delamination in package forming and packing operations.

There is no special difference between the properties of the laminates containing the same type of plies and produced by different methods. This can be illustrated upon the basis of the data for laminates produced by the German company Kalle by use of extrusion and dry bonding technique. (Table 8)

Very thin layers can be achieved by extrusion coating.

The thickness of the proper layer decides about the barrier properties, not the lamination technique. The substance of dry bonding laminates is slightly higher (presence of adhesive layer).

For quality control of ready made laminates it should prove to be useful to consider the most frequently encountered defects in lamination process including the method of their elimination. (Table 9)

SUMMARY OF THE RESULTS OF CHECKING BOND STRENGTH OF THE LAMINATES

Measurements at peeling angles 180 and 90° TABLE 6

Type of laminate		Unprinted laminates – Peeling angle 180°				90°			
		IMADOS		COBRO		IMADOS		COBRO	
		$\bar{x}$ /N/	V_x%	$\bar{x}$ /N/	V_x%	$\bar{x}$ /N/	V_x%	$\bar{x}$ /N/	V_x%
Al/paper (wax lamination		0,55	4	0,63	6	0 70	7	0,77	I0
Al/parchment(wax lamination)		I,02	I0	0,78	8	I,I0	5	0 68	4
Cellophane/cellophane (wax lamination)		0,06	33	-	-	0,43	23	-	
Cellophane/AL/PE (dispersion adhesive)		2,20	8	2,20	8	3,I5	5	3,00	6
Cellophane/Al/PE (dispersion adhesive)		1,40	23	I,10	II	I,48	II	2 27	6
Cellophane/PE/Al (extrusion lamination)		0,97	30	0,26	27	0,36	28	0,44	36
PETP met/PE	dry bonding polyurethane adhesive	I,2I	2I	I,16	I3	0,79	I4	I,43	I0
" "		I,5I	I4	I,25	II	I,43	34	I.43	5
" "		I,02	I0	0,58	8	0,80	5	0,4I	4
PA/PE		X		3,52	3	X		5,56	5

V_x variation coefficient

"-" means that measurement was not conducted

"X" means that separation of the layers was not possible

SUMMARY OF THE RESULTS OF BONDING STRENGTH OF SANDWICH PRINTED LAMINATES

Measurements at peeling angle 180 and 90° TABLE 7

Type of laminates	type of printing	Sandwich printed laminates Peeling angle 180°				90°			
		IHADOS $\bar{x}$ /N/	$V_{x\%}$	COBRO $\bar{x}$ /N/	$V_{x\%}$	IHADOS $\bar{x}$ /N/	$V_{x\%}$	COBRO $\bar{x}$ /N/	$V_{x\%}$
celofan/celofan wax lamination	Evita	0,11	50	0,04	25	0,28	14	0,21	24
cellophane/Al/PE dispersion adhesive	Fenix	0,69	36	0,67	31	0,78	24	1,08	30
cellophane/Al/PE dispersion adhesive	Kava	1,20	18	1,08	11	1,80	13	1,82	7
cellophane/PE/Al extrusion lamination	Kava	0,76	21	0,56	41	0,30	80	0,34	35

Table 8

Comparison of the properties of laminates made by the use of extrusion coating and dry bonding technique /xx

Type of the laminate	Thickness	Substance ±10%	Yield appr.	Tensile strength		Elongation		Range of heat sealing temp.	Range of application temp.	Permeability for gases 20°C;0% rel.Hum./xx			Water vapour permeability 20°C ; 80% rel.hum.
	µm	g/m²	m²/kg	N/cm		%		°C	°C	cm³/m² ·24h·bar			g/m² · 24h
				MD	TD	MD	TD			O₂	CO₂	N₂	
cellophane-PE extrusion 30/10	32	41	24,4	30-40	20-35	20-25	50-80	130-200	0 to 80	ca 20	ca200		ca 10
cellophane-PE dry bonding 30/25	47	55	18,2	30-40	20-35	20-25	50-80	130-200	0 to 80	ca 20	ca200		ca 4
Cellophane-PExx extrusion 35/75	97	101	9,9	30-50	25-35	18-25	50-70	130-200	0 to 80	ca10	ca20	ca10	ca 0,6
Cellophane-PExx dry.bondring 35/75	97	102	9,8	30-50	25-35	20-25	50-80	130-200	0 to 80	ca10	ca20	ca10	ca 0,6
Hostaphan-PE extrusion12/20	32	35	28,5	25-30	25-30	70-130	70-130	130-200	-60to80	ca100	ca450	ca24	ca 2,5
Hostaphan-PEextrusion 12/50	62	63	15,9	25-30	25-35	70-130	70-130	130-200	-60to80	ca100	ca450	ca24	ca 1,6
Hostaphan-PE dry bonding 12/50 xxx	64	66	15,2	25-30	25-35	70-130	70-130	130-200	-60to90	ca100	ca450	ca24	ca 1,6

x/ Kalle Folien „Datenblatt"

xx/ with exception of cellophane combinations for which relative humidity = 43%

xxx/ Hostaphan - Company's name for polyester films

Appendix 3

Quality Control Tests Conducted under the Supervision or according to the Suggestions of the Adviser

I. Determination of Al layer thickness of metallized laminates
2. Bond strength measurements of different types of laminates
3. Measurements of elasticity modulus of flexible materials
4. Control of barrier properties of flexible laminates previously subjected to standard crushing
5. Procedure used for evaluating substance of particular layers of the laminates
6. Tests for control heat sealibility of coated flexible materials
7. Impact dart drop test as a method for control of polyethylene film quality used for frozen food packing
8. The use of impact dart drop test for strength measurements of packaging papers
9. Impact drop test in applications to already filled bags and pouches
I0. Evaluation of tearing strength of plastic films
II. Quality control of shrink and stretch films
I2. Quality control of ready made rolls of flexible materials
I3. Out of flatness measurements
I4. Systems of sampling of flexible materials

Appendix 4

Measurements of the Elasticity Modulus and 1% Modulus of Plastic Films

$$E = \frac{\sigma}{\varepsilon} = \frac{Po/\ Ao}{\Delta l/l} = tg\, \alpha$$

E - elasticity modulus (Young modulus)
stress (σ) to strain (ε) in this part of stress - strain curve, when straight proportion between these values exists (region of elastic deformation)

Po - force involving increase " Δl" of the sample of preliminary length "l" and initial cross section "Ao" (region of elastic deformation)

Elasticity modulus for some films is difficult to measure (difficulties in finding the best fitted tangent in the preliminary part of stress - strain curve for determining the inclination of the initial part of this curve)

For practical purposes in quality control of plastic films so called I% modulus ($E_{1\%}$) or in other words secant or apparent modulus is the most frequently used.

$$E_{1\%} = \frac{\sigma}{\varepsilon} = \frac{P/Ao}{\Delta l/l} = \frac{P/Ao}{1/100} = \frac{P/Ao}{0,01} = \frac{P \cdot 100}{Ao}$$

Example of measurements conducted with CETEA staff for polyethylene terephtalate film of 0,0I2 mm thickness and I5 mm width

Attached diagrams achieved at following conditions
scale 2 kG
machine speed I cm/min
paper speed I0 cm/min
I mm of elongation at I00 mm distance between the jaws of strength measuring machine corresponds to I% elongation (I0 mm on paper scale)

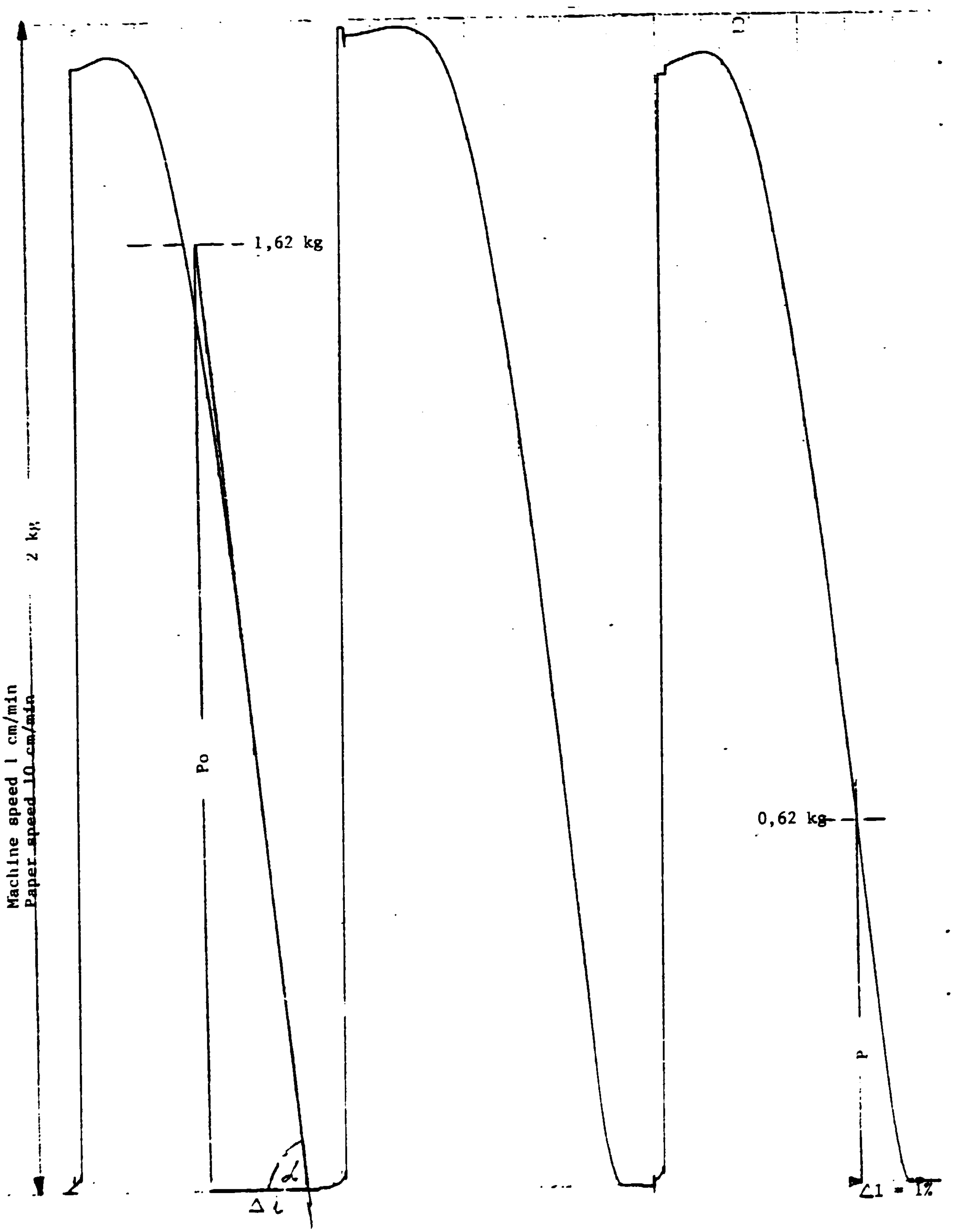
Ao = t x w
t - initial thickness of the sample
w - initial width of the sample

t = 0,0I2 mm
w = I5 mm

Ao = 0,0I2 × I5 = 0,I8 mm

$$E = \frac{\dfrac{I{,}62}{0{,}I8}}{\dfrac{2}{I00}} = \frac{I{,}62 \times I00}{0{,}I8 \times 2} = \frac{I{,}62}{0{,}36} = 450\ \mathrm{kG/mm}^2$$

$$E_{1\%} = \frac{\dfrac{0{,}62}{0{,}I8}}{\dfrac{I}{I00}} = \frac{0{,}62 \times I00}{0{,}I8} = 344\ \mathrm{kG/mm}^2$$


1,62 kg
2 kg
Machine speed 1 cm/min
Paper speed 10 cm/min
Po
α
Δl
0,62 kg
P
Δl = 1%

The Method Used for Control Water Vapour Permeability of Crushed Flexible Materials.

6 samples of the dimensions I20 x I20 mm should be cut out from the tested materials. On each of them at an equal distance from the edges the squares I00 xI00 mm should be drawn - this determines the edges of the further heat sealing.

Each of the samples should be tightly wound up on auxiliary rod (I0 mm diameter). The rod is then taken off and the edges of the sample are fixed with the use of self adhesive tape.

Rods (10 mm diameter), made e.g. of copper, are introduced to a depth of 45 mm (on both sides) to both sides of the rolled sample. In this position the rods are fixed by means of self adhesive tape.

The sample prepared in this way is placed on the hard and flat surface of a table. Crushing is realized five times, drawing the rods closer to one another, what takes place at a distance of 30 mm. The sample is then unwound and from two samples of this kind a flat bag is formed by heat sealing.

The internal size of the bag should be equal to I00 x I20 mm.

The bag is filled with 30-40 g of dried calcium chloride and is instantly sealed according to the previously drawn line.

The internal dimensions of the bag (between the sealing) should be equal to I00 x I00 mm.

The excess of the material on the exterior side of the heat sealing should be cut off. The width of heat sealing should not be less than 3 mm.

At least 3 bags of this type are prepared for each type of analysed material.

The bags are put to the chamber of constant temperature 38°C at relative humidity 90%. The bags are weighed on an analytical balance until constant increases are achieved.

These increases are calculated in traditional system for checking water vapour permeability in $g/m^2 \cdot 24$ hours.

As a result the average value of all measurements for each analysed material is given.

SPECIFICATION OF THE FILMS USED FOR LAMINATION

Specification for PA films.

I. Types

In dependence on application two types of PA films can be listed:

F For laminates used for thermoforming

NF For laminates used as a cover of thermoformed packages and for pouches making

2. Requirements

2.I.I. Typical thickness and acceptable deviations

Type	Thickness µm	Acceptable deviation µm
NF	20	± 2
NF and F	30	± 3
F	40	± 4
	50	

2.I.2. The width of PA film used for lamination should be IO mm wider than the width of the pressing roll.

2.2. Appearance

Film should indicate uniform transparency without any mechanical damages, foldings and so on. The edges of the film should be cut properly without any damages. The hardness should be uniform along the width of the roll. The winding up core should not be deformed.

2.3. Hazness of the film is determined for F type only and may be considered as an ability of the film for thermoforming.

Thickness µm	Haze %
30	3
40	4
50	6

2.4. Quality of ready made roll.

Film should be tightly wound up without any foldings. The side planes of the roll should create a perpendicular surface to the axis of the winding up core. Acceptable displacement of following layers should not exceed ± 2 mm.

2.5. Out of flatness.

Out of flatness should not exceed 0.3%.

2.6. Sensoric evaluation

Transmission of substances changing the taste and odour of drinkable water should not take place to a higher degree than determined as very slight when checking after 24 hours immersion.

3. Storing the film before lamination.

The rolls of PA film should be overwrapped by LDPE film (50 - 80 µm) and sealed with self adhesive tape. The excess of the film should be pressed inside the core.

Specification for Polyester Films PETP.

1. Typical thickness and acceptable deviations
   Typical thickness of PETP films is equal to 12 and 15 µm with acceptable tolerance of ± 1 um.
2. Appearance
3. Quality of ready made rolls.
4. Out of flatness
5. Sensoric evaluation

Similar requirements as in the case of PA films.

6. PETP films should be overwrapped in thin PE film protecting agains the entry of dust to the surface of the film.

Specification of PE and PP 9unoriented) films.

1. Typical thickness and acceptable deviations
   Typical thickness covers the range 50 - 70 µm with acceptable tolerance of ± 5 µm of the medium thickness.
2. Width of the film

Generally speaking the width of PE or PP films used for lamination with PA or PETP films should be 15 - 20 mm wider than the width of the last-mentioned films. The acceptable tolerance from the nominal width should not exceed ± 2 mm.

3. Appearance
4. Quality control of ready made rolls
5. Out of flatness

Similar requirements as in the case of PA films.

6. Surface tension (degree of treatment)

The side of the film foreseen for lamination should indicate (just before lamination) a surface tension of not less than 38 mN/m (dyne/cm).

7. Senseric evaluation

Transmission of the substances changing the taste and odour, checked with the use of milk chocolate as a standard product, should not take place to a higher degree than determined as very slight in the intensity scale given in the testing method described in Attachement 1.

8. Storing the films

Films should be wrapped in thin PE overwrap protecting against entry of dust to the surface of the film. The film can be stored as long as the surface tension value does not fall below the value 38 mN/m.

ATTACHMENT I

TESTING METHODS APPLIED FOR EVALUATION OF THE FILMS USED FOR LAMINATION TO BE CHECKED BY THE MANUFACTURER OF THE LAMINATES.

I. Thickness shoud be controlled with use of a device apt to measure with accuracy of ± 0,5 µm. The lower measuring surface has to be plane with a diameter between 3-6 mm, pressure on the sample should remain in the range 50-200 kPa(500-2000 G/cm^2).

2. Haze

Haze of PA films should be checked according to ASTM D I003-6I Method A (with the use for example of a Gardner Laboratory Hazemeter). Haze should be checked, using 10 samples cut from 2 pieces of the film and taken from the roll in I m distance from one another. The arithmetical medium is taken as a result.

3. The general qualityof the roll should be checked on the basis of visual observations and measurements of the displacement of the layers with the use of the slide gauge.

4. Ouf of flatness is controlled according to the method described below.

4.I. Application

The method is used for films and laminates especially foreseen for machine packing, lamination or printing.

4.2. Definition

Out of flatness is defined as the degree of geometrical deformation of the film or laminate, expressed as percentage difference between the longest and the shortest sample divided by the length of the shortest sample, these samples being cut from a 2500 mm long sheet of the film.

4.3. Equipment

4.3.1 The table

A flat table, 2700 mm long and 1000 mm wide, with smooth surface and well leveled, should be used for the tests.

At one side of the table a straight line, called preliminary line, is drawn parallel to the width of the table. At the second end of the table paper with a millimeter-scale, covering the distance between 2400 - 2600 mm from the preliminary line, is sealed.

At the same side of the table a reed of 10 mm diameter is fixed, above which the samples cut from flexible materials are hung. (Figure 1).

4.3.2 Angle gauge with the length of the shoulders of not less than 500 mm.

4.3.3. Guillotine for cutting the samples.

4.3.4. Self adhesive tape.

4.4. Preparation of the sheet of the materials for testing.

On the unrolled piece of the film two lines are drawn at a distance of 2500 mm from each other, perpendicular to one of the edges of the film. The tested material is cut from one side according to the drawn line, and on the other side approximately 400 mm above the second line. The places of highest and lowest deformations are observed and marked at the side of the samples which will be hung over the reed. The example of a roll with deformation on one side and the different lengths of the samples cut from such a roll are illustrated in Figure 2.

4.5. Cutting the samples.

Samples are cut with the use of a guillotine in the previously marked places of maximum and minimum deformation. The width of the sample is equal to 10± 2 mm.

In the case that any visible deformation is observed, the sample should be cut from both edges and the middle of the web. The material should be rolled before cutting. The cutting knife should remain in exactly perpendicular position to the rolled material. A non-durable deformation of the sample can take place during the cutting.

At least 3 samples should be prepared for each measurement. Samples should be cut and checked not later than 2 hours after unwinding of the film from the roll.

4.6. Testing procedure.

Samples of the film should be put on the table one beside the other and parallel to the longer edge of the table. The ends of the samples, cut according to the drawn line (on the film) should be placed exactly on the preliminary line of the table and sealed by means of self adhesive tape. The opposite ends of the sample should be put over the fixed reed and loaded with a weight of 20 g each. This allows to eliminate different types of foldings to take place on the samples. Directly after loading of the sample the length of the measured segment should be determined with an accuracy of up to ± 0.5 mm.

4.7. Calculation of the results.

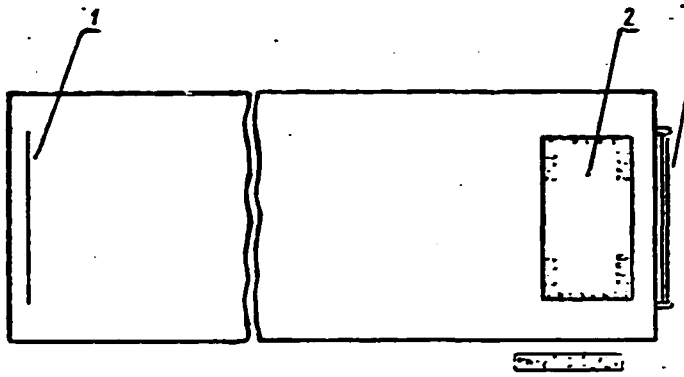
Out of flatness (OF) in % can be calculated with the help of the formula:

$$OF = \frac{l\ max - l\ min}{l\ min} \ 100$$

l max - the length in millimeters of the longest sample

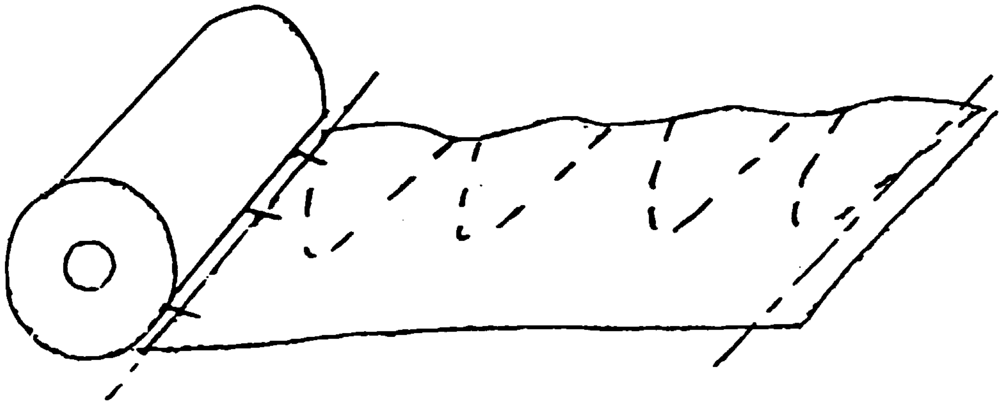
l min - the length in millimeters of the shortest sample

Figure 1 THE VIEW OF THE TABLE USED FOR OUT OF FLATNESS MEASUREMENTS

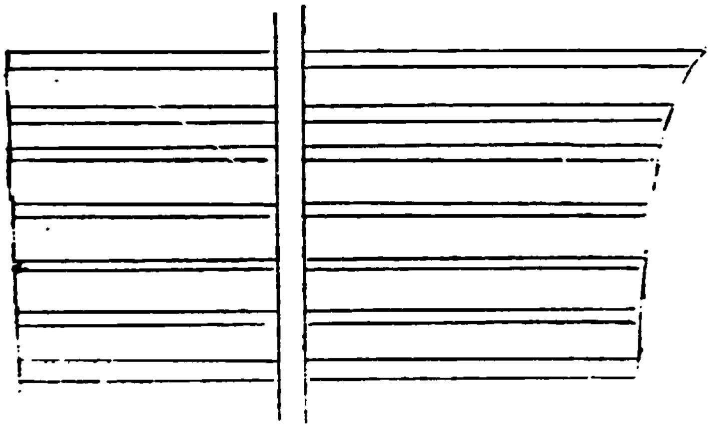


1 - Preliminary line
2 - Paper with millimeter scale
3 - The reed for hanging up the samples

Figure 2



The roll of the material with deformation on one side



The lenght of the samples cut from different places of the roll shown above

Appendix 7

SPECIFICATION FOR LAMINATES PRODUCED BY DRY BONDING TECHNIQUE.

I. Appearance

The surface of the laminate should be smooth without foldings and foreign matters. The plies of laminates should be joined uniformly along the whole surface without any places not completely sealed, without stains and bubbles.

The edges should be carefully cut without any mechanical damages. Cutting of the edges can take place not earlier than 5 days after the lamination, and heat sealing at least 10 days afterwards.

2. Resistance for separating of the layers (bond strength).

If preliminary separation of the plies is possible, the force required for further delamination should not be less than:
I50 cN/I5 mm for sandwich printed laminates
200 cN/I5 mm for PETP/PE and PA/PP
300 cN/I5 mm for PA/PE laminates(excluding sandwich printing).

3. Ability for thermoforming.

Ability for thermoforming is determined for F type laminates foreseen for deep drawing. This type of laminates should allow deep drawing in dependence of the laminates thickness up to the depth:
30 mm for PA/PE 30/70 F
40 mm for PA/PE 40/70 F
50 mm for PA/PE 50/70 F
At the same time the thickness of a standard package formed with the use of a standard tool and measured in the middle of its edges should not be lower than 30% of the preliminary thickness of the laminate(Figure I)
Any separation of the plies as a result of thermoforming is acceptable.

4. Quality of the roll.

The roll should be tight without any foldings, it should have a uniform hardness along the whole web. The head of the roll should create a perpendicular plane with the axis of a rewinding core. Acceptable displacement of the single layers of the laminate or part of the layers should not exceed ± 1 mm, when the material is already finished and cut to the required final dimensions.

5. Sensoric evaluation.

Transmission of the tase and odour changing substances to the drinkable water should not take place to more than what can be considered a very slight degree.

In the case of sandwiched printed laminates the triangle test should be conducted after 48 hours of immersion of the sample in water and after 24 hours for all other types.

6. Solvent retention.

Solvent retention evaluated by chromatographic method should not exceed 4 mg/m^2 (assuming that ethyl acetate or methyl-ethyl-ketone were used as the solvents in the lamination process.

TESTING METHODS USED FOR EVALUATION OF READY MADE LAMINATES

I. Bond strength measurements

In the case of laminates combined with polyurethane adhesives the sheet of laminates of the dimensions allowing to cut in machine direction IO samples I5 x I50 mm each is immersed to the depth 1 - 2 cm into the mixture of solvents containing ethyl acetate, toluene and acetone in the proportion 1 : 1 : 1, for 24 hours.
After this, by cutting with a razor one of the layers of laminate and levering with the scalpel the piece of the cut layer, delamination is started.
In the case of a negative result of delamination, the edge of the laminate is immersed into the heated mixture of dimethyl formamide and xylene in the ratio I : I for a few seconds.
Before conducting the tests, preliminary delaminated samples should be conditioned.
After conditioning the delaminated samples are fixed in the jaws of the strenght measuring machine at a distance of approx. 40 mm. Beginning of non delaminated sample should be maintained in equal distance from both jaws.

Starting distance between the jaws is equal to 50 ± 1 mm.

Delamination is conducted on 40 mm length of the laminate at the speed of 100 mm/min with simultaneous registration of the force in the function of the distance of delamination.
On the diagram achieved, the axis of the force is divided into equal parts. With the accuracy of 1 cN the value of delamination force is read out

$$(P_1; P_2; P_3; P_4; P_5; P_6; P_7)$$

presuming that P_1 should be read out at 30% and P_7 at 90% of the length of the diagram.
The bonding strenght of the laminate "R" is calculated in cN/cm as the medium value from the formula:

$$R = \frac{\sum_{i=1}^{i=7} P_i}{7 \cdot b}$$

$P_1 - P_7$ ..... values of bonding force from the diagram
b .... width of the sample in cm.

2. Ability for thermoforming of PA/PE and PA/PP laminates.

The ability for thermoforming can be checked with the use of a laboratory type vacuum forming machine with a working surface of not less than 260 x 400 mm. The dimensions of the standard tool used for checking thermoformability of laminates is illustrated in Figure 1. The tool should consist of exchangeable elements, allowing to form different depths as indicated in the specification of PA films.

During the preliminary tests the optimum thermoforming conditions should be determined (heating time and temperature at which the best reproduction of the shape of the forming tool is possible without overheating the laminate).

The tests are conducted with the application of three samples cut from the middle part of the web. The dimensions of the sheet for thermoforming should be adjusted to the size of the frame of the vacuum forming machine.

Each forming "blister" should be used for cutting the samples of 10 mm width, and for checking the thickness in two places.

The places for cutting the samples and thickness measuring points are given in Figure 1.

Results are calculated from the formula:

$$C = \frac{a_1 + a_2}{2} \cdot \frac{100}{b} \ \%$$

C = Thickness in measuring points as a percentage of the preliminary thickness of the laminates

a_1; a_2 = Thicknesses in the measuring points of the expected highest reduction of the thickness

b = preliminary thickness of the tested laminate

3. Sensoric evaluation of laminates.

The same testing procedure should be applied as in the case of sensoric analysis of the films used for lamination.

4. Control of solvents retention.

Principle of determination.

Gas chromatography with use of the head space technique is applied for solvent retention testing. Any type of gas chromatograph with flame-ionization detector can be used in these tests.

In this method the sample of the laminate is heated in a closed glass jar for 30 minutes at a temperature of 115°C. The sample of the solvents is taken from the jar in the phase of vapour by means of a gas-tight syringe.

The amount of laminate applied in these measurements should be fixed in such a way that for 1 cm^3 of the volume of the glass jar 1 cm^2 of the controlled laminate should be used. In the case of printed laminates the sample should be selected in such a place that the covering with prints and the amount of colours is representative for the whole web of the film.

Samples of laminate should be cut in 30 mm wide stripes.

Conditions of testing (to be considered as an example only)

- Steel analytical column
  (2 m long, Ø - 4 mm) filled with Chromosorb G (0,I6-0,20 mm) containing 5% of polyethylyglycol advpinate (Carbovax I540)
- Temperature of separation 80° C isotermin conditions
- Carrying gas - nitrogen at a flow rate of 30 cm^3/min
- Identification of the amount of solvents is determined by means of internal standard at the same conditions applied as in the case of tested samples.

5. Sensoric analysis of the film used for lamination.

The trial starts with an introductory test. In this test the sample of the film is tightly closed in a glass flask (I cm^2 of the film per I cm^3 of the flask volume).

If after 24 hours only very slight odour is perceptible no other tests are made and it is assumed that the films are acceptable.

It was found that addition of a small amount of water to the flask(approx. 0,2% of its volume) facilitates identification of odour presence.

If after this time the presence of odour is considered more than slight, a typical sensoric analysis by means of the triangle method is made. For this purpose 200 cm^2 of the film is cut to pieces and is placed to the conical flask of 0,5 dcm^3 volume which is filled with 200 cm^3 of the water. The flask is tightly closed. Eventual change of odour and taste of the water is checked after 24 hours in room temperature. The intensity of changes of the odour and taste of the water is evaluated on the basis of a three points scale:

- very slight but perceptible changes
- easily percebtible change
- significant change (easily perceptible)

6. Evaluation of the surface tension of PE and PP films.

Evaluation of the surface tension is undertaken by means of standard solution with known surface tension or by use of an equipment allowing to measure the contact angle formed between the surface of tested film and the drop of a standard liquid.

For checking the surface tension of polyolefine films solutions of fixed concentration of mono-ethyl ether, of glycol ethylene and formamid are usually used.

Details of the testing procedure are given in the Draft of International Standard ISO/DIS 8296.

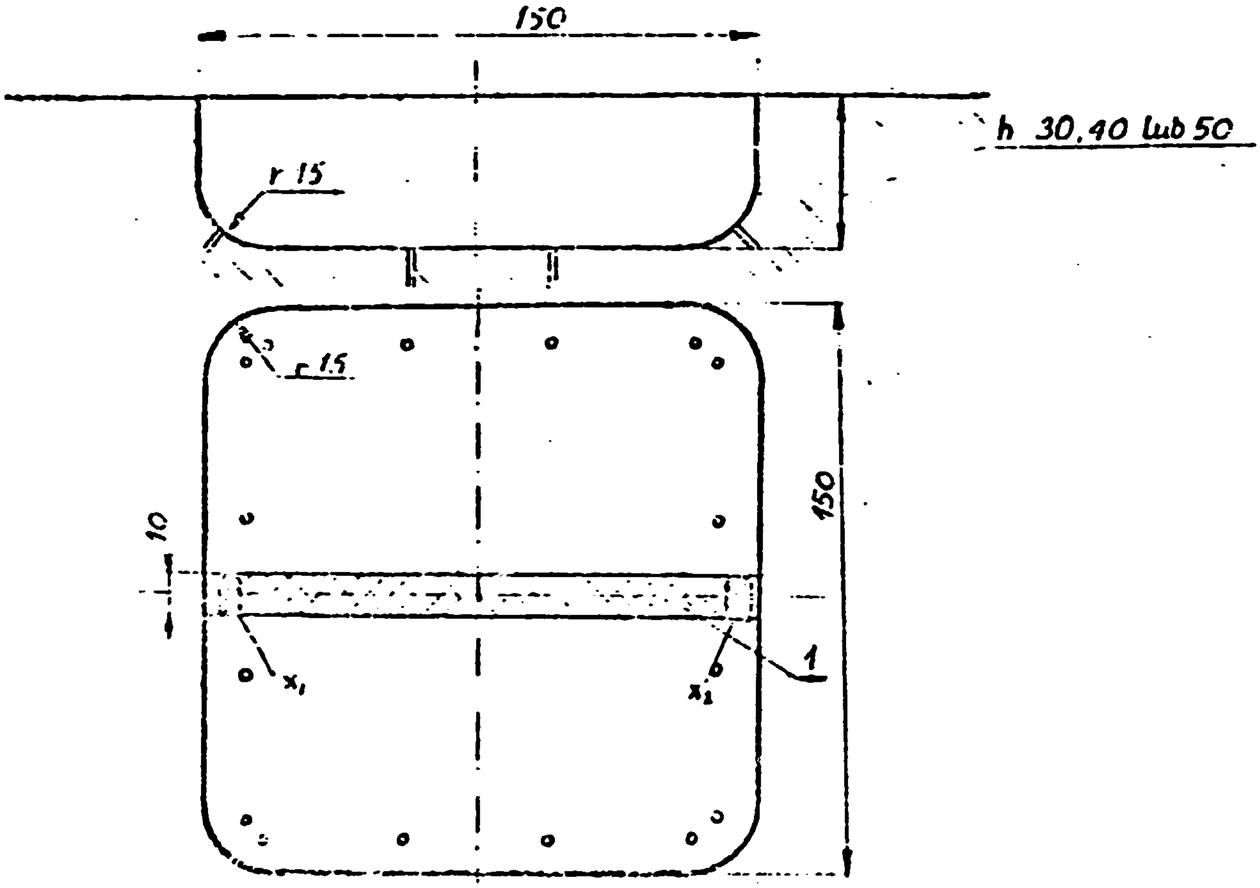


FIGURE 1.

Dimensions of standard tool for vacuum forming of laminates with PA layer.

1. Location of cutting samples from thermoformed shape and displacement of thickness measuring points.

Appendix 8

The threshold values for the solvents most frequently used in production of flexible materials, determined by the method of dilution factor

pos.	type of the solvent	Threshold value of the solvent, expressed in dilution unit
I.	2-methylacetamid	I : I00
2.	isopropanol	I : I20
3.	n-hexen	I : I500
4.	2-propylene glycol	I : I700
5.	acetone	I : 2I00
6.	methanol	I : 8000
7.	ethylene glycol ether	I : 8000
8.	benzen	I : 9000
9.	n-propanol	I : I5000
I0.	ethanol	I : 20000
II.	trichloroethylene	I : 35000
I2.	n-octan	I : 40000
I3.	cyclohexanone	I : 50000
I4.	four-hydrofurane	I : 80000
I5.	isobutanol	I : 80000
I6.	n-butanol	I : I00000
I7.	methyl isobutyl ketone	I : I50000
I8.	methyl ethyl ketone	I : I50000
I9.	ethyl acetate	I : 200000
20.	toluene	I : 200000
2I.	octanol-I	I : 400000
22.	iso-amyl alcohol	I : 400000
23.	n propyl acetate	I : 400000
24.	ethyl benzene	I : 800000
25.	2 propylene ketone	I : 900000
26.	cyclohexanol	I : I000000
27.	n butyl acetate	I : I500000

Appendix 9

A.Polymerization residuals

I.Monomer

The tolerated level varies from 0 for acrylonitryle (PVDC copolymers, poliacrylonitryl, ABS) to I - 2 % for caprolactam.

2.Initiators (source of free radicals, peroxides or hydroperoxides)

a)soluble in water(not soluble in monomer),mainly inorganic, used for emulsion polymerization of PVC, PVDC, Polyvinyl acetate, styrene and its copolymers, ethers

hydrogen peroxide
ammonium, sodium, potassium, persulfates
t-butyl hydroperoxide }
cumene hydroperoxide } PS

b)soluble in monomer, mainly organic (not soluble in water) used for suspension, sometimes for bulk or solution polymerization

Types: peroxydicarbonates
ketone peroxides
Alkyl peroxides
Acyl peroxides
peroxyesters

Examples:
di(4-t-butyl cyclohexyl)peroxy carbonate }
di(sec-butyl)peroxydicarbonate (the last one also used for MDPE) }
Diisopropyl peroxydicarbonate }
benzoyl peroxide PVC,PS } PVC and other vinyl polymers

t-butyl perbenzoate }
di-t-butyl perbenzoate } PS

di-t-butyl peroxide }
t-butyl peroxyacetate }
t-butyl peroxypivalate } LDPE

3.Catalysts and cocatylysts

Policondensation reactions - simple acid or bases are used

Cationic polymerization - most often $Al\,Cl_3$, $AlBr_3$, $SnCl_2$, BF_4(electrons acceptors)

Cocatalysts - $H^{\oplus}$ donors

Anionic polymerization - LiH_4, Li alkyls, Na aryl and alkyls, NaH_2 (electron donors)

Ziegler-Natta catalysts - most often chlorides and bromides of titanium and vanadium + organoaluminium or organozinc compounds

Examples: ($TiCl_4$ +/iscbutylo/$_3$ Al) }
($TiCl_4$ +/etylo/$_3$ Al } HDPE, PP

4. Reaction transfer agents (moderators) terminate the growth of the polymeric chain (usually donors of hydrogen)

mercaptans e.g. dodecyl mercaptane
xantogenates
chloroalkanes e.g. tetrachloride carbon (PS, PP, PE)
Thiokols
also hydrogen (LDPE) Acids as phosphoric, acetic, adipic - policon densation of polyamides

5. Emulsifiers (in emulsion polymerization)

Types: (a) anionic (most popular) e.g. stearates, palmitates, oleates of sodium, potassium, ammonium, aromatic sulfonic acid salts (PVC, PS)
(b) cationic e.g. quaternary ammonium salts $(N(R)_4)Cl$
quaternary phosphites salts $((RO)P)Cl$
(c) non-ionic e.g. esters of glycerol and fatty acids, PAW, condensation products of ethylene oxide and fatty acids, alkohols, phenoles (PVA)

6. Emulsion stabilisers and dispersion stabilisers (protective colloids)

gelatine, PVA, methyl cellulose, sodium mettacrylate, carboxymethyl cellulose
inorganic: silicates, talc

7. pH buffers

phosphates, sodium carbonate or acetate
(used mainly in emulsion polymerization)

Furthermore, polymer might be contaminated by solvents used in the reaction as aromatic or aliphatic hydrocarbons (PP), paraffin and paraffin oil (LDPE). In general only emulsion polymerization produces a significant level of impurities in polymer, 2-4 o/o. Other methods, especially bulk polymerization, yield a relatively pure polymer, although even even quantities which are irrelevant from the hygienic point of view can worsen for instance light and thermal stability or processing.

B. Additives

I. Antioxidants

Two basic types: (a) primary or chain-terminating antioxidants (transfer of hydrogen from NH,- or OH-reactive group to free radical)
The most popular types are secondary aryl amines and hindered phenols, which in turn can be divided into simple phenolics as BHT (3,5-di-t-butyl-4-hydroksytoluene)

BHA (2-t-di-butyl-4-hydroxyanizol)
2,6-di-t-butyl-peresol
bisphenolics as 2,2-(4,4'-dihydroxy-diphenylo)-propane
polyphenolics
thiobisphenolics as 2,2'-thio bis-(4-methyl-6-t-butylphenol)

Examples of amine-type antioxidants:

N, N' diphenyl-p-phenylenadiamine

(b) secondary stabilisers - decomposing of peroxides
Usually phsophorus or sulfur containing compounds as phosphites and thioesters.

Examples: tris (mononomylphenyl) phosphite } phosphites
distearyl pentaerythiol diphosphite }
tetracis (2,4-di-t-butylphenyl) 4,4'-biphenylene-diphosphonite
dilauryl thiodipropionate } thioesters
distearylthiopropionate }

The common practice is to combine two types of antioxidants to get a synergistic effect.

Polyolefines stablilization:
Theoretical sensitivity for oxidation,
conntected with branching PP>LDPE>HDPE
↘ ↙
actually inverse because
of higher level of residual
catalyst

LDPE - requires from 0.001 to 0.1 % low molecular weight antioxidant as BHT or BHA

PP, HDPE - low molecular weight phenolics as BHT are used to aid processing and higher molecular weight phenolics for long term stabilisation, combined with thioethers and phosphites as synergists. These polymers require higher level of antioxidant 0.1 - 0.5 %.

Styrenics stabilisation: PS alone is not susceptible for thermal oxidation (but susceptible to UV). Little, if any, antioxidant is required, simple phenolics as BHT + TOP (trioctadecylphosphite) + DLDTP (dilauryl thiodipropionate). HI polystyrene is more prone for oxidation due to butadiene double bond, intermediate molecular weight phenolics are used in combinations with phosphites.

Amount 0.1 to 0.3 %

ABS - very susceptible for oxidation. Three-component systems are commonly used.

phenolic }
phosphite } up to 1 %
thioester }

Typical liquid phosphite is used - tris (mono-nonyl-phenyl) phosphite which serves also as emulsifier.

Other polymers like PA, PETP, do not usually require antioxidants in higher amounts. Depending on the application, when needed the same types are used, i.e. phenolics, amines and organic phosphites.

2. Heat stabilisers

Used primarily for PVC and essential for this polymer (processing).
Also used for other halogenated polymers.

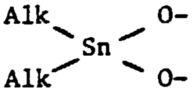
Lead compounds - stearates, phosphites and recently phtalates, moleates, silicates and sulfates are of longest use, but not acceptable for food contact applications.

Ba/Cd stabilisers as stearates and other organic and inorganic salts in different combinations are of widest use, but also not sanctional for food contact.

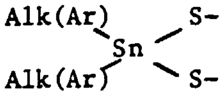
Zn/Ca stabilisers - organic salts as stearates or laurates are less effective than before but generally accepted to a certain level for food contact application.

Note: Commercially available salt-stabilisers are specific combinations of different compounds, up to ten and even more (synergism). They can contain other metal compounds and costabilisers, usually of organic nature.

Organotin stabilisers: generally two classes - alkyl derivates containing oxygen bonds



and alkul or aryl derivates containing sulphur



Examples: Dibutyltin dilaurate
Dibutyltin dimaleate
Dioctyltin dimaleate*

*Di-n-octylin -s,s¯bis (isooctylmercaptoacetate)

Specific organotin stabilisers are approved for food contact in many countries as designated by*. In general, dialkyl and diaryl organotin compounds are regarded as nontoxic contrary to trisalkyl and trisaryltin.

Other stabilisers:

Many other compounds are used as stabilisers, e.g.:

diphenylene thiourea
esters of aminocrotonic acid
polyhydric alcohols
tertiary phsophites
epoxy compounds (octyl epoxy stearate)
nickel chelates

Their stabilising efficiency is comparatively low and there is a tendency to use them as secondary or auxiliary stabilisers with mixed metal ("primary") stabiliser blends.

3. Lubricants

Mostly used for PVC. Divided into external (friction between metal parts and polymer) and internal (friction between polymer chains). Typical lubricants for PVC are glycerol fatty acids esters.

	Internal	External
Degree of esterification	low (oleate)	high (dioleate)
Chain length	low (C_{11})	high (C_{18})

Other lubricants for PVC:
fatty alcohols (C_{11} - C_{13})
metal soaps - costabilizing effect in PVC
(stearates) used for their release properties for PS, PE, PP, ABS, rubbers
fatty acids amides - PVC, ABS, PE, PP, BS (also slip agents)
paraffin - PVC, rubber
polyethylene - rigid PVC

Other glycerol partial esters are used. In PE, PP and PS they also act as release agent. High molecular weight polyolefines require paraffin wax or polyethylene wax for better processing.

4. Plasticizers

About 75 % of plasticizers are used for PVC.

Basic types: phtalates: Di(2-ethylhexyl)phtalate (DOP)*
Dibutylphtalate (DBP)
Butyl benzyl phtalate (BBP)
Diisodecylphtalate (DIDP)

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* in some countries approved for food contact applications

Adipates: di(2-ethylhexyl)adipate (DOA)*
benzyloctyladipate
di(cyclohexyl)adipate

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*sanctioned by FDA
good low temperature performance

Sebacates: di(butyl)sebacate*
di(octyl)sebacate

---

*sanctioned by FDA
good low temperature performance

Azelates: di(n-hexyl)azelate
Citricates: tris(butyl)citricate
tris(ethyl)citricate
acetyl-tri-n-octyl citricate

Aliphatic dicarboxyacid esters are generally recognized as non-toxic and most of them are approved for food contact.

Epoxy compounds: epoxidized soybeen and linseed oils, epoxidized octyl tallate or oleate accepted for food contact, also have stabilising properties ("secondary stabilizers")

Other popular plasticizers: organic phosphates, but generally not sanctioned for contact with food.

Secondary plasticizers for PVC: aromatic and aliphatic oils, chlorinated paraffins, chlorinated polyethylen

Plymeric plasticizers: (gaining popularity because of low migration level)
adipic acid esters
phtalic acid esters
sebacic acid esters
e.g. poli(propyleneglycol adipate)
nitrile rubbers - copolymers of butadiene and acrylonitrile

Plastification of other polymers:

Polyvinylacetate: lower phtalates (dibutyl, diethyl, citricates, diethylene glycol dibenzoate)

Cellulose nitrate, Acetate-propionate + Butyrate: lower alkyl phtalates, also phosphates because of their flame retardance.

Polivinilidene-chloride: dibutyl sebacate, acetyl-tri-n-butyl citrate. phtalates not recommended because of migration.

PS - rarely to one percent of low polarity plasticizer as butyl oleate

HDPE, PP - to improve impact polymeric plasticizers are used like butyl rubber of ethylene/propylene rubber

5. UV absorbers

Basic types: 2-Hydroxybenzophenones, e.g.: 2,4-dihydroxybenzophenone
2-hydroxy-4-n-octyloxybenzphenone
Hydroxyphenol benzotriazols, e.g.: 2-(2-hydroxy-3,5di-t-amylphenyl)benzotriazol
2-(2¯hydroxy-5¯methylphenyl)benzotriazol
Salicylates, e.g.: phenyl saliccylate
4-t-octylphenyl salicylate
Substituted acrylates, e.g.: dimethyl 2-(4-metoxybenzylidene)malonate
methyl-2-carbometoxy-3-(p-metoxyphenyl) acrylate

Nickel chelates are also used as well as hindered amines and piperidines.

Main application: polyolefines. Benzophenones, benzotriazoles and hindered amines are commonly used for these polymers.

PVC - not susceptible for UV radiation, when needed benzophenones and benzotriazoles are used.

PETP- not susceptible. Sometimes benzotriazoles are used.

Cellulosics - aryl esters (rezorcinal, monobenzoate), salicylates mainly, sometimes benzophenon and benzotriazols.

PS - poor resistance to photooxidation. Benzophenones, cyclic amine and benzotriazols are used. HI PS - additionally antioxidants.

ABS- very susceptible. Benzophenones and benzotriazols.

Carbon black also acts as UV protecting agent by absorption and dispersion of solar energy.

6. Mold release agents

Metallic soaps (calcium, magnesium, stearates)
PVC, PS
Waxes, silicones, fluoroplastics.
Also external lubricants act as mold release agents.

7. Antistatic agents

Quaternary ammonium salts: most effective but not approved for food contact
Amine derivates, especially ethocylated amines: approved for food contact
derivates of polyhydric alcohols, often etoxylated alcohols
Phosphate esters and polyglyca esters of fatty acids.
Essentially compounds containing hydrophilic and hydrophobic (polymerphilic) parts, that create the conductive path on the surface of the polymer after migration.

8. Slip additives

Oleamide: amide ololeic acid
Erucamide: amide of erucic acid
Stearamide: amide of stearic acid

Mainly used for polyolefines, but also for other thermoplastics as PS, ABS. The agents listed have food contact approval. Sometimes they are used as mixtures to achieve the desired blooming time.

9. Antifogging additives

Fatty esters,for instance glycerol compounds
Linear alkul ($C_6 - C_{12}$) phtalates, used as plasticizers, also have antifogging properties. Antifog and Antistat effects are often achieved by the same compound, because of very similar action.

10. Antiblocking additives

Typical antiblocking agents include polysiloxanes, silicates (e.g. aluminium silicate) or silica in particles 1-2 µm.

11. Blowing (foaming) agents

- azo compounds
  - diazoaminebenzene
  - azobisisobutyronitrile
  - azodicarbon amide
- N nitroso compounds
- N,N' Dimethyl N,N' dinitrosoterephtalamide
  - sulphonyl hydrazines
- Benzene sulphonyl hydrazine
- Toluene 4 sulphonyl hydrazine

SEMINÁRIO Appendix 10

ASPECTOS TÉCNICOS SOBRE FABRICAÇÃO E APLICAÇÃO DE MATERIAIS FLEXÍVEIS D EMBALAGEM.

Palestrante: Dr. Bohdan Czerniawski - consultor da ONUDI em materiais flexíveis de embalagem para alimentos.

Idioma: Inglês

Data: 03/05/85 **Taxa:** Cr$ 50.000,00

PROGRAMA

08:00 - 09:00 - Inscrição

09:00 - 09:30 - Apresentação das Atividades da Área de Polímeros e Celulósicos do Projeto BRA/82/030 - ITAL.

09:30 - 10:00 - Centro Polonês de Pesquisa e Desenvolvimento de Embalagem: atividades e cooperação com industrias.

10:00 - 10:15 - Café

10:15 - 12:00 - A influência do Processo de Fabricação nas Propriedades Básicas de Materiais Flexíveis de Embalagem, especialmente de Estruturas Laminadas.

12:00 - 14:00 - Almoço

14:00 - 15:45 - Materiais Flexíveis Metalizados: situação atual e tendências.

15:45 - 16:00 - Café

16:00 - 17:30 - Filmes Encolhíveis versus Filmes Esticáveis: competição ou, coexistência?

17:30 Coquetel

List of used abbreviations

Al	aluminium
BOPP	bioriented polypropylene
cello	cellophane
CETEA	Packaging Food Technology Centre (Brazil)
COBRO	Polish Packaging Research and Development Centre
EMA	ethylene methacrylate copolymer
EVA	ethylene vinyl copolymer
FDA	Food and Drug Administration
HDPE	high density polyethylene
IMADOS	Cechoslovakian Institute of Manipulation Storing and Packing
ITAL	Institute of Food Technology (Brazil)
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
MDPE	medium density polyethylene
met	metallized
MFI	melt flow index
pap.	paper
PAV	polyvinyl alcohol
PE	polyethylene
PETP or PET	polyethylene terphtalate
PP	polypropylene
PS	polystyrene
PVA	polyvinylacetate
PVC	polyvinylchloride
PVDC	polyvinylidene chloride
r.h.	relative humidity
UV	ultra violet
4/D	length/diameter