BIOS FINAL REPORT No. 445
ITEM Nos. 9, 22

INVESTIGATION OF GERMAN PLASTICS PLANTS
PART III.
PROCESSING OF POLYVINYL CHLORIDE

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE
LONDON - H.M. STATIONERY OFFICE

12377 - Wt. 49182 - Dd. 5447

INVESTIGATION OF GERMAN PLASTICS PLANTS

PART 3.

PROCESSING OF POLYVINYL CHLORIDE

15 September - 23 October
1945

Reported by:

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T. Love M. of S.

B.I.O.S. Target Numbers -

22/40, C22/2339, C22/2043, C22/2015, C9/580, C22/1201, C22/2305, C22/2040, C22/2016.

BRITISH INTELLIGENCE OBJECTIVES SUBCOMMITTEE

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- PART III -
PROCESSING OF POLYVINYL CHLORIDE"

A M E N D M E N T

Page 47, third line from bottom of page - (Fig 41) should read (Fig 42.)

INVESTIGATION REPORT

on

B.I.O.S. Trip No. 1193

Group 3.

Investigating Team Personnel -

J.W.C. Crawford	M. of S.
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Targets investigated -

Dynamit A.G.	Troisdorf, near Köln. Krümmel, near Hamburg.	22/40. C22/2339.
Deutsche Linoleum Werke	Delmenhorst, near Bremen.	C22/2043.
Schlieper & Baum A.G.	Wuppertal/Elberfeld	C22/2015.
Deutsche Grammophon G.m.b.H.	Hannover	C9/580.
Bisterfeld & Stolting	Radevormwald, near Wuppertal.	C22/1201.
Paul Troester	Hannover/Wülfel.	C22/2305.
Joseph Eck & Söhne	Düsseldorf/Heerdt.	C22/2040.
Hermann Berstorff	Hannover/Buchholz	C22/2016.
Maschinenban Anstalt G.m.b.H.		

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A. Calendered sheet from polyvinyl chloride.

1. Dynamit A.G., Troisdorf, near Siegburg, Rhine Province.

Interviewed: Dr. R. Röhm, Director, in charge of the Mipolam Department of the Plastics Section.

During an earlier visit to Troisdorf (C.I.O.S. Trip 458, June 1945), members of the party had interviewed Dr. Röhm on the subject of processing of polyvinyl chloride and related plastics. A number of points of interest had arisen out of this visit which made a further visit desirable, and Dr. Röhm was now interviewed again. Information obtained covers the fields of calendering of sheet, production of cable masses, and new work on the direct extrusion of polyvinyl chloride. The information has been reported under these headings.

In addition to the information obtained from Dr. Röhm during interviews, the writers had the opportunity of extracting information from a commonplace file of works recipes and procedures, of current date, referring to Mipolam Department processes. For greater clarity this has been collected as a series of appendices to the present report.

Polyvinyl chloride raw materials used at Troisdorf.

Polyvinyl chloride. The material used is I.G. Igelit PCU, straight polyvinyl chloride made by the emulsion process. The PCU came from each of the three I.G. factories making it, and the properties varied mainly because of the method used to prepare the solid PCU from the emulsion in which it was formed. In making Ludwigshafen or Schkopau material the emulsion is either coagulated and after continuous filtration and washing, the polymer is dried with hot air in a continuous belt drier ("Imperial" process); or the emulsion is sprayed on to heated rolls and the film of polymer scraped off, continuously ("Escher-Wyss" process).

At Bitterfeld, the emulsion is evaporated in a spray drier ("Nubilose" type) by contacting the sprayed emulsion with hot air.

In Ludwigshafen or Schkopau material, the particle size is within the range 0.1 - 1 mm; in the Bitterfeld material, these particles have been sintered, under the influence of the hot air, into hollow spheres simulating the original emulsion spray particle, and about 100 mu. diameter. The surface size and texture of the particles affect greatly the behaviour of the PCU with plasticisers. Ludwigshafen and Schkopau polymers gelatinise rapidly, whilst Bitterfeld material is slow in taking up the plasticiser. This difference in behaviour calls for different treatments when plasticised PCU is being made.

For production of plasticised PCU material, the polymer used has K value about 70 (PCU grade G); for unplasticised products, the K value is 60 - 65 (PCU grade A).

It was stated that the normal package for PCU was 50 Kilo bags made of jute "Kaschiert" with Mipolam paste, but stocks seen at Troisdorf and at Krümmel were packed in paper bags.

Wacker polyvinyl chloride. This polymer (Vinnol) was not normally employed by Troisdorf, but evidence was obtained from the Research Department files that in comparative tests of laboratory prepared plasticised sheets, Wacker's material showed superiority over the I.G. in some respects. The comparison is detailed in Appendix 1.

Vinyl chloride interpolymers. Apart from experimental quantities of other vinyl chloride interpolymers, the interpolymersused at Troisdorf are those employed to make "Astralon" a clear celluloid-like sheet material used generally in place of the latter, over which it has a number of advantages, particularly non-inflammability. The same interpolymers are used for moulding and for production of low-softening, easily worked cable-covering masses.

The range of interpolymers of this type used at Troisdorf has already been given in Part 2, but is repeated below.

Name and use.	Composition	K value	Price to Troisdorf from I.G.Ludwigshafen (R.M. per Kilo : 28.7.44)
Igelit MP Grade A (Astralon)	80 vinyl chloride 10 ethyl maleate 10 methyl maleate	55 - 60	2.30
Igelit MP Grade K (wire covering)	84 vinyl chloride 16 methyl acrylate	72	1.60

Name and use.	Composition	K value	Price to Troisdorf from I.G. Ludwigshafen (R.M. per Kilo: 28.7.44)
Igelit MP Grade AK (unplasticised for mouldings)	80 vinyl chloride 10 methyl acrylate 10 isobutyl maleate	70	1.60
Igelit MP Grade D (Astralon)	80 vinyl chloride 20 methyl acrylate		1.60

The grade A polymer is preferred to the original Igelit MP (Grade D) on account of better flowing properties on the calender rolls, in addition to advantages already mentioned.

Igelit MP is manufactured at Ludwigshafen. According to how the dispersion of the interpolymer has been processed to obtain the solid resin, the latter comes as a fine powder (Escher-Wyss process) or as chips (Imperial process). These drying processes are described in C.I.O.S. Report File XXIX, No 62.

Types of calendered polyvinyl chloride made at Troisdorf

The polyvinyl chloride calendered sheet made at Troisdorf is classified as follows :-

Hard Mipolam, Vinidur. Sheet rolled and calendered from unplasticised polyvinyl chloride (Igelit PCU)

Soft Mipolam. Sheet made from plasticised polyvinyl chloride -Igelit PCU, usually straight, sometimes with a little (5%) Igelit MP added to improve workability.

Astralon. Sheet made from unplasticised interpolymers of the Igelit MP type.

Processing of Igelit to Mipolam sheet.

The processing can be divided into three sections :

1. Preliminary mixing of ingredients.

2. High temperature rolling in mixing mills, to complete mixing and thermoplasticise the plastic.

3. Calendering to give the final sheet.

In the case of Astralon sheet, the calendered product usually requires hot press polishing to give a satisfactorily smooth finish. Soft Mipolam calendered on to cloth, for upholstering purposes, is subsequently embossed with a design in embossing presses (see Appendix 4).

1. Preliminary Mixing.

(a) Unplasticised Igelit PCU and MP.

With unplasticised PCU, it may be necessary to incorporate lubricant and stabiliser, although the polymer was also bought with these already incorporated. Where it is necessary to carry out the mixing, the components are mixed in bowl mixers, or in the Petzhold Kreisalmischer described in Part 2. This machine is claimed to be very effective in rapidly dispersing small amounts of material throughout the mass of Igelit. It has a large working capacity, 300Kg.

Ceresin wax, 1.2 - 2.0%, is used at present as lubricant for unplasticised PCU. Octadecyl alcohol, now unobtainable, was formerly used. Both lubricants have about the same effectiveness.

The stabilisers normally used at Stabiliser I (J) - alpha phenyl indole, and C (diphenyl thiourea) . The quantity added is around 0.5%. The stabiliser discolours the polyvinyl chloride mass during milling through its own oxidation.

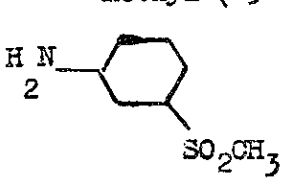
Stabiliser which discolours cannot be used for Astralon. In this case 2% of methanol (on the weight of Igelit MP) is added to the mixer. The use of methanol is the subject of a patent by Röhm and Fikentscher to I.G. (Germany and U.S.A.).

In addition to the preceding stabilisers, the following stabilisers have been used at Troisdorf.

Stabiliser	Composition	Price to D.A.G., 28.7.44 RM/Kilo
P	Phenoxy propylene oxide	4.50
DBG	Di-isobutyl phenyl glycidyl ether	5.75
HRA (AH)	Adipic acid dihydrazide	15.-
BS	Butadiene sulphone	9.-
-	Thiodipropionic acid hydrazide	15.-
1	alpha - Phenyl indole (ex Leverkusen)	8.50
C (Vulkacit) CA II	Diphenyl thiourea	
MPTH	Monophenyl thiourea	

Besides the products mentioned above two experimental samples from Ludwigshafen were found at Troisdorf. Analysis showed them to be

Stabiliser A methyl (3- amino phenyl) sulphone,



Stabiliser D 4,4' - diamino - diphenyl sulphone

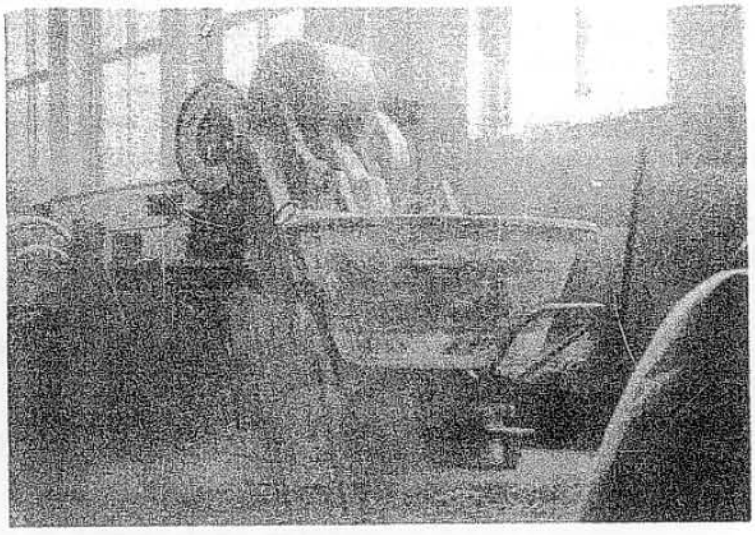


Fig. 19

Fig. 20

mixer. The product from this procedure was claimed to be a sandy mass, easily handled, and satisfactory for rolling. The use of a temperature of 50 - 60° was said to avoid gelatinisation.

While no inconsistency is necessarily present, it should be noted that the Werner-Pfleiderer mixing procedure differs from that given in items in the commonplace file, referring to the production of plasticised PCU masses - see Appendices 2 and 5.

In these cases, the mixture of PCU and plasticiser is heated at 130-150° in a mixer till gelatinisation commences (angelatiniert). The use of this high temperature mixing was observed during a visit to Deutsche Linoleum Werke, Delmenhorst (q.v.); the product coming from the Werner-Pfleiderer mixer was in this case a tough, rubbery mass, showing that considerable gelatinisation had taken place.

Pigments. When present, pigments are incorporated in the mixer with PCU and plasticiser, being added last. Where pastel shades are sought, the pigment is firstly dry mixed with PCU, e.g. in the Petzhold mixer, to obtain maximum uniformity.

2. High temperature rolling.

The premixed composition is mixed on heated rolls to complete conversion to a homogeneous, thermo-plasticised mass ready for calendering.

Troisdorf use only mixing rolls for compounding the premixed Mipolam masses. Dr. Röhm was asked for his views on the Banbury mixer. He stated that they had experimented with Banburys and were favourably impressed by them. He would like to have installed them, but the machines were scarce in Germany: all supplies of them were allocated to Buna processing. He made the point (generally realised) that the large mount of frictional heat generated in the Banbury was a disadvantage, for in the hands of an inexperienced or careless operator decomposition of the polyvinyl chloride could result from overheating.

Troisdorf rolls. The standard Troisdorf rolls for compounding of Mipolam sheet masses are comparatively small, due probably to the amount of manhandling the product gets during the processing. They have been described in Part 2 and their principal measurements and power consumption are given in Appendix 2. Hot water under pressure is used for heating the rolls.

During the rolling of hard Mipolam and of Astralon, dust rises from the rolls when fresh powder is added, and with soft Mipolam, the usual vaporisation of plasticiser occurs. Troisdorf have a comprehensive suction ventilation system, by which ducts lead to hoods built over the rolls, to extract fumes rising from them. The hoods are glazed with Astralon sheeting, which appeared a desirable feature, giving better illumination of the work.

As has been previously mentioned, the bearings of the mixing rolls are cooled by cold water circulating in canals cast or machined in the bronzes, and lubrication is by circulating oil, fed to the bearings by a pump. Dr. Röhm stated that it was not absolutely necessary to water cool the bearings, but doing so notably increased their life. During the war, bearing metal was scarce and bad, and even plain cast iron bearings had been used. Much trouble had been caused with bearings of rolls and calenders by the use of unsuitable oil.

For mixing Mipolam, the friction ratio between the rolls does not exceed 1.3, and may be unity.

Rolling of hard Mipolam. This has already been dealt with in Part 2, but the following notes are of interest.

Hard Mipolam sheet can be calendered comparatively rapdily, and four rolls are employed to provide the feedof mixed material; when scrap hard Mipolam is being reworked, five rolls are used. The technique used may vary considerably according to conditions: the following seems to be typical :--

The roll nearest the calender, and that behind it are the finishing rolls, in which the mass is brought to the final stage of plasticity. On the first roll of the series, fresh PCU is rolled into a sheet. Strips of the sheet, weighingabout 6 Kg, are cut off from time to time and fed to roll 3. Meanwhile on roll 2, scrap hard Mipolam is being similarly sheeted again, and strips from these rolls are also added to roll 3. Processing of the sheet from roll 3 to roll 5 is also carried cut by cutting off strips, not the whole sheet, and such strips from roll 5 are fed to the calender. The procedure has the advantage of giving a more even progress of the material through the rolls and to the calender. In the case of the first rolls, it is an advantage to have thermo-plasticised material already on the rolls when adding fresh PCU powder, as the latter adheres to the plastic material. Even so a good deal drops out on the first passage: it is swept up by a hand brush and shovel and replaced on the rolls.

The output rate is 2,000 Kg of hard Mipolam in 8 hours.

The transference of the strips of Mipolam from one roll to the next was done by hand, and the process was not imposing from the point of view of labour usage. Some remarks of this kind were made to Dr. Röhm, who made the point in reply that whilst it was appreciated that the process was wasteful in labour, so long as a man had to stand over the rolls during the mixing, cutting and turning the sheet to get good incorporation, he might as well be doing the additional work of cutting off and carrying to the next roll. If mechanisation were to be introduced, it should cover the mixing operation as well as the transference of the product. Troisdorf were interested in this problem of mechanisation of the mixing process, but development of ideas had been hindered by the necessity furing the war for maintaining full output from the existing plant.

Since admittedly the rolling plant had been staffed by Russian women during the war, the economic disadvantage of the current procedure would not have been likely to cause concern to D.A.G. On this point of foreign labour, it was stated that the Russian women were capable of obtaining greater output than the German men workers employed earlier. At the time of the present visit, the rolling was being done by unskilled German workers, and was giving little satisfaction.

Rolling of soft Mipolam. As has been stated in the earlier report, the normal service of mixing rolls is three per calender. This however refers to the production of calendered sheet of normal thickness for raincoats - about 0.12 mm. When thick sheet (the maximum being 1.4 mm.) is being calendered, four rolls may be needed. If scrap is being reworked, another roll is required to handle this. The procedure is generally similar to that described for hard Mipolam. It was stated that the output from 3 rolls was 500 Kg in 8 hours. 12 - 15 Kg of composition are carried per roll.

Rolling of Astralon. The procedure is generally similar to that for soft Mipolam, with three rolls normally in service, four when reworking scrap.

Direct extrusion of premixed soft Mipolam into calender. An interesting experimental setup for doing this was seen. A normal extrusion machine as used for cable mass was mounted, with its motor, on a frame provided with wheels to make it moveable. The usual die had been replaced by a slit die, about 6" wide by $\frac{1}{8}$" deep, made of stainless steel. The die was heated by an electrical winding. In use, the machine was wheeled up to the calender feed, and mass from the Werner-Pfleiderer mixer extruded directly into the nip of the calender rolls. Results had been

encouraging, but wartime conditions had not permitted of this experiment being further developed.

Calendering

Five calenders, with their mixing rolls (about 20) occupy the Mipolam shop. This building is approximately 200 feet long by 60 feet wide by 27 feet high, lighted from roof and sides.

Calenders. The calenders in the Mipolam shop are as follows :

Made by H.Berstorff, Hannover --

No.1	1000 x 450 mm.	4- bowl	Delivered before 1936
No.2	1350 x 600 "	3- bowl	" 1938
No.3	1650 x 700 "	4- bowl	" 1940
No.5	1800 x 750 "	4-bowl	" 1942

Made by J. Eck, Düsseldorf --

No.4 1650 x 700 mm. 4-bowl

The Eck calender is provided with that firm's form of skew-setting (Schrägstellung) of three of the rolls (Nos. 1, 2 and 4). The Eck, like the Berstorff 4-bowl calenders, has roll 1 behind roll 2, and rolls 3 and 4 mounted above 2. The mass fed in thus lies in the trough between two horizontally disposed rolls. The calender follows established practice for polyvinyl chloride calenders in having watercooled bearings. When seen, it was in use to produce hard Mipolam sheeting to be employed in acid-resisting linings for chemical plant at Chemische Werke Hüls.

The Berstorff calenders were not provided with skew-setting devices, and the rolls were all parallel ground. The bearings were water-cooled.

Calenders are provided with small draught hoods situated over the top rolls and connected to the suction ventilation system (see fig. 21). The rolls are heated by steam, as the hot water system was inadequate to maintain the temperatures required. Hot water heating is preferred, and it is desired to be able to maintain a temperature of 200°.

Power for driving the calenders is supplied by 3-phase 50 cycle 380 volt A.C.motors, driving through change-speed gearboxes. The rolling speeds obtainable are approximately 4,8, 11 and 15 meters per minute. The first three speeds are obtained by gear change; the fourth by field regulation. The 3-bowl Berstorff with rolls 1350 x 450mm., has a 110 KW motor, and uses 60 KW when rolling soft Mipolam of 0.12 mm. The 4-bowl Berstorff with rolls 1800 x 450 mm. has a 150 KW motor.

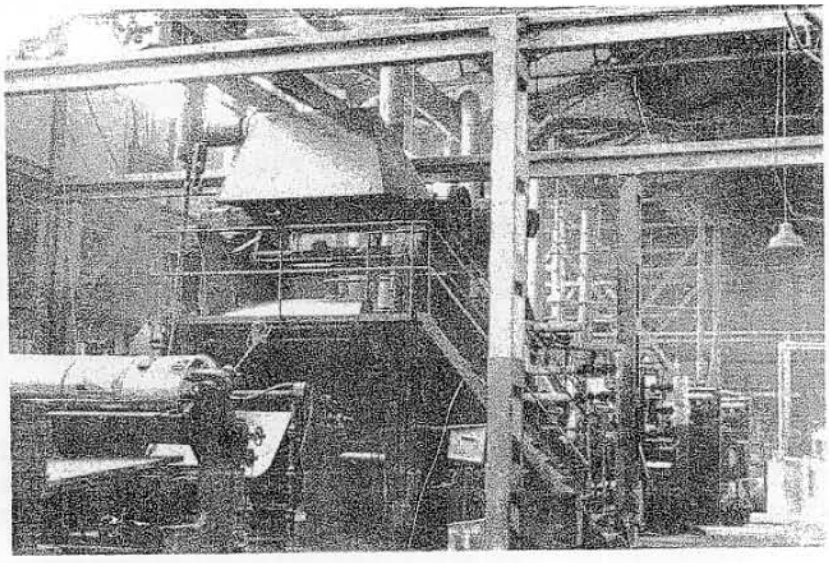


Fig. 21. Ventilation of Mipolam calenders, Troisdorf.

In all cases, the calender rolls have even speed. Friction has been tried, but even speed is preferred.

Three bowls are enough for calendering soft Mipolam, but four bowls give a better finish. Mipolam can be calendered on to base cloth in a three-bowl calender; the cloth is run through the second nip. Four bowls are used for doubled cloth (See Appendix 3).

Shape of calender bowls. Under rolling stresses, the calender bowls bow slightly, producing a sheet which is thicker in the middle than at the edges. Dr. Röhm was asked about use of camber on the rolls to counteract this bowing. He stated that Troisdorf had tried rolls which had been cambered (bombiert) by grinding slightly barrel shaped. The difficulty was that a given camber was correct only for a given composition working under given conditions of temperature, sheet thickness, etc., and after trials, Troisdorf had reverted to parallel (cylindrical) ground bowls. It was claimed that soft Mipolam sheet 0.12 mm. thick could be calendered to a variation of 10 - 20 mm over the width, using cylindrical rolls.

The question of the value of skew-setting (Schrägstellung) was discussed. Eck had well publicised their invention for skew-setting the bowls, and as the reason for doing so seemed very plausible, Troisdorf had purchased their 4-bowl Eck calender. Their experience with it had however been disappointing. The skew-setting had been found in practice to be "spongy", so that it was impossible to skew the rolls to a definite amount, or keep the amount of skew fixed. Eventually the rolls had been set back with their axes parallel and the machine used as a conventional calender.

Despite this unsatisfactory experience, Dr. Röhm was still of opinion that skew-setting was basically sound, and should give good results once the mechanics of effecting skewing had been put right. The Eck calender delivered to Troisdorf was of wartime manufacture and the workmanship and material in the bearings was poor. It will be appreciated from the notes on the visit to Eck that with the type of bearing used by them for skew-setting, poor workmanship could easily produce the sponginess of setting of which Dr. Röhm complained.

Simple flexing of the bowls under the stresses of rolling produces a sheet of lenticular section shown greatly exaggerated as

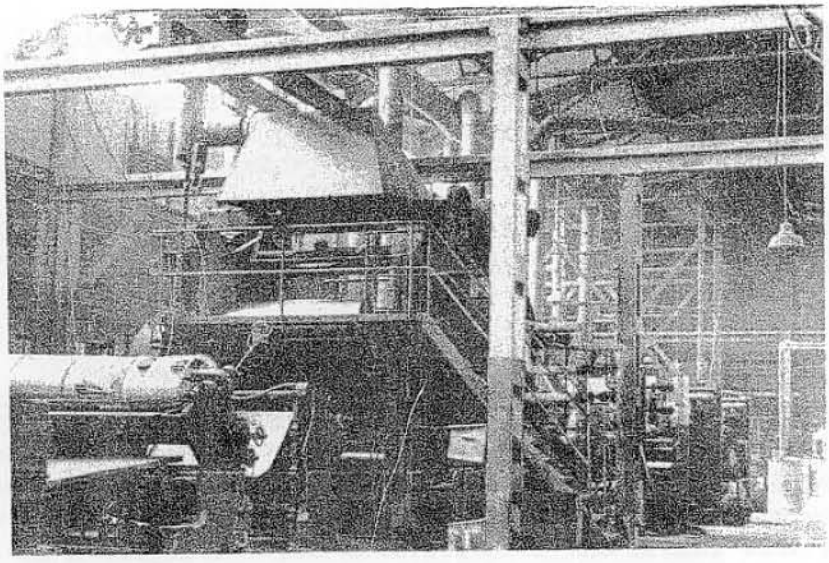


Fig. 21. Ventilation of Mipolam calenders, Troisdorf.

2. Deutsche Linoleum Werke, Delmenhorst.

Deutsche Linoleum Werke is a large factory situated in the town of Delmenhorst, 8 miles west of Bremen. As the name implies, the principal concern of the factory is the production of linoleum, but a section is devoted to production of calendered Mipolam; we are indebted to Mr. Claxton, U.S. investigator, for information on this point.

Personnel interviewed were Herr Ludwig Kaufmann, technical director of the factory, and Herr Rohlfs, works engineer in charge of the Mipolam department.

Production data. The Delmenhorst factory has a maximum capacity for Mipolam of 225 tonnes per annum of finished goods. This capacity is mainly thin calendered sheet, such as is used for raincoats, but some shoe sole Mipolam was also made, in sheets 4- 5 mm. thick. Production of the latter was mainly carried out by another D.L.W. factory at Bietigheim, near Stuttgart. The activities of the D.L.W. with Mipolam date from 1937.

Calendered Mipolam sheet

Starting materials.

Polyvinyl chloride. Most of the PVC used is I.G. material, drawn from either Schkopau or Ludwigshafen. Bitterfeld (spray dried) material was not normally used, except for the low grade, cheap waste material obtained on cleaning out the Nubilose spray drier. The following comments on the working properties of PVC were given by Herr Rohlfs.

The Schkopau PVC was much finer powder than the Ludwigshafen, took up the plasticiser more smoothly, and stood high rolling and calendering temperatures better (i.e. with less decomposition). Bitterfeld regular material was as satisfactory as Schkopau, but the waste Bitterfeld material, a hard granular product, was generally rather unsatisfactory. The rolling temperature used for Schkopau was 160°.

In addition to the I.G. polyvinyl chloride, Wacker's polyvinyl chloride (Vinnol HH) was also employed. D.L.W's opinion of this material was similar to those we had already heard. It could be worked in the same apparatus as the I.G. material, but required more care. Presumably on account of its known higher viscosity, it required a higher temperature on the rolls - 170° - and the working range of temperature was narrow: a rise of only 5° would cause rapid blackening of the mass on the rolls.

Stabilisers. Stabilisers are not added to the Mipolam compositions.

Plasticisers. The following table lists the plasticisers which D.L.W. had employed, together with comments on their behaviour supplied by Herr Rohlfs --

Trade name and maker	Chemical Composition	Comments
T.C.P Heyden, Dresden	Tricresyl phosphate	Gives high tear resistance and tensile strength. Cold resistance -5° to - 10°; volatility, 3%
Mesamoll Grade I. I.G.,Merselburg	Phenolic ester of sulphonated Fischer-Tropsch aliphatic hydrocarbons	Good plasticiser. No smell Bluish fluorescence. Little or no colour. Good weather resistance. Volatility 3%. Cold resistance - 10°.
Palatinol F I.G.Ludwigshafen	Phthalate of Leuna alcohols C_6 - C_8.	Cold resistance -20°
Palatinol ES I.G.,Ludwigshafen	Phthalate of Leuna alcohols, C_8 - C_{11}	Good plasticiser. Gives very clear films, which remain colorless on ageing (T.C.P. and Mesamoll films colour somewhat).
Palatinol UV I.G., Ludwigshafen	Leuna C_6 alcohol phthalate	Used only experimentally; no manufacturing data or experience.

Trade name and maker	Chemical Composition	Comments
Plastomoll KF	Triethylene glycol ester of "forerum" synthetic fatty acids ex Fischer wax.	Cold resistance -30°. Not weather resistant. 1 year exposure to weather gives films brittle through leaching of plasticiser.
ED 356 Märkische Seifenindustrie Rossleben, Dessau	Phthalate of Leuna alcohols C_5- C_6	Like Mesamoll in general properties.
IW 36 Märkische Seifenindustrie	Triethylene glycol ester of "forerun" fatty acids	Cold resistance -40°, but very volatile (20%).
Mesamoll I.G.Uerdinger	Hexanetriol ester of "forerun" fatty acids	Not good - poor plasticising action, poor weather resistance.
Diamyl phthalate		

* Sample of film heated 4 days at 100° in air oven, and loss in weight measured.

Filler. Chalk is used as a filler but only in very small amounts - approximately 3% on the composition.

Colours. I.G. organic dyestuffs pastes have been tried, but are very dear, and not satisfactorily resistant to sunlight. At present, all colours employed are inorganic, including those for transparent Mipolam sheeting. The following colours were given --

Chrome yellow
Chrome green } Vassen, Aachen

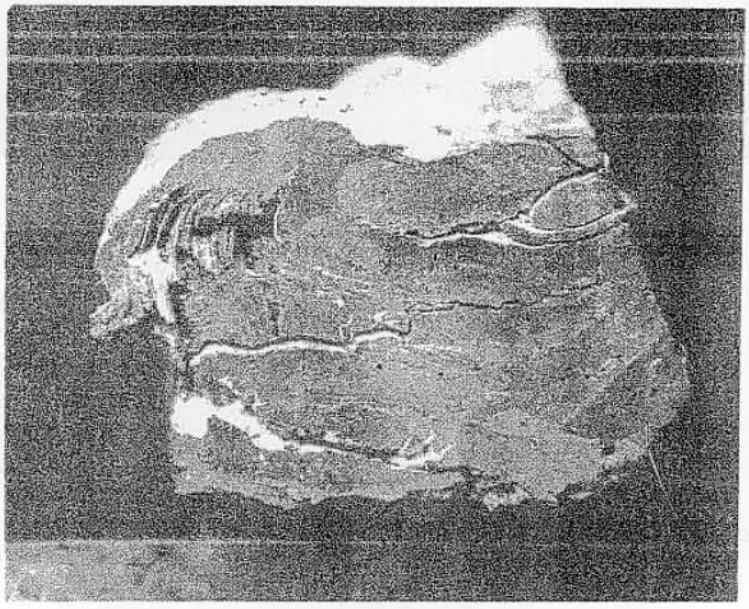


Fig. 22

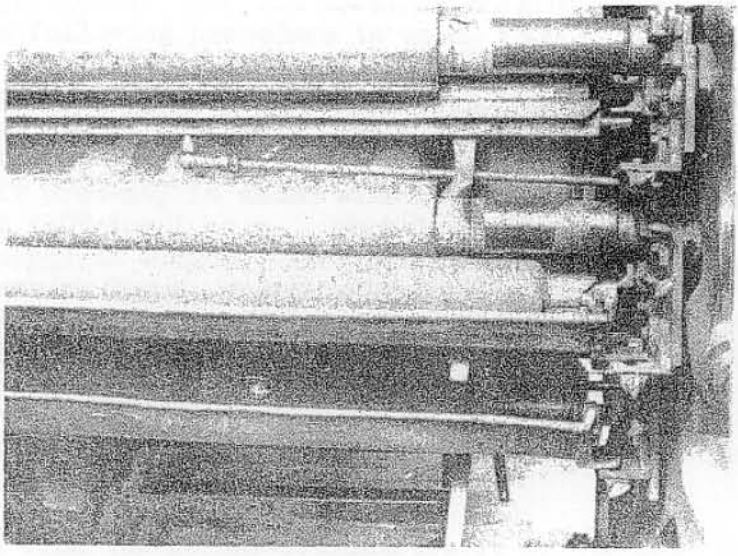


Fig. 23

Iron oxide, red and yellow, I.G. (very good)

Blue Bright ultramarine, I.G. Leverkusen
Paris blue, Gebr. Siegler, Stuttgart

White Titanium oxide, I.G.

The inorganic colours were said to show satisfactory resistance to sunlight.

Mixing of compositions.

The PVC : plasticiser ratio is between 50:50 and 60:40. All mixing is done in large iron steam jacketted Werner-Pfleiderer mixers with sigma blades. These were bought second-hand, and had been originally used in chocolate manufacture. For 50:50 mixtures, the incorporation is done at room temperature. For the usual calendered sheet formula (approx. 60:40), the following procedure is used (300 Kilo charge) -

The plasticiser is weighed out and introduced into the Werner - Pfleiderer, which has been preheated. The plasticiser is brought up to 140°, and when at this temperature, the PVC is introduced in a few minutes. Colour, if present, is added with the PVC. After this, the mixture is worked at 140° for 1 hour. Shortly before completion, a little chalk (whitening) is added. This is to break the contents of the mixture into discrete lumps, prevented from sticking together by the chalk. The blades are then reversed, the machine tilted and emptied into large flat pans on castors. Examination of the product at this stage showed it to be tough, free from discrete plasticiser, gelatinised, at least in part; the mass was in layers, separated by interfaces at which was whitening. Fig. 22 shows a section of a lump; the laminated structure should be noted.

Rolling. The mass from the Werner-Pfleiderers is rolled into sheet. To do this, use has been made of existing horizontal mixing rolls, formerly employed for reworking scrap linoleum mass. Two pairs of rolls are used per set, the material receiving two rollings.

The general German practice is to use very little friction on Mipolam mixing rolls; these linoleum rolls on the other hand have pronounced friction - front roll, 35 r.p.m., back roll, 8 r.p.m. - and in order to avoid trouble with decomposition the rolling procedure differs from normal, in that only one pass is given, and the sheet is unusually thin.

B. Printing of calendered soft Mipolam sheet.
Schlieper and Baum A.G., Elberfeld.

This firm of calico printers and textile finishers has two factories, at 22-40 Wupperstrasse, Elberfeld, and at Laaken. Mipolam work is done at Elberfeld only.

The newer and larger calico-printing shop lost its roof and received other damage during the disastrous raids on Elberfeld. The machinery has suffered greatly by exposure to the weather.

The older shop has had its roof repaired, and the machinery used for printing Mipolam printing is here. It is normal calico printing machinery.

Personnel interviewed were:

Dr. Baum
Herr G.A. Baum } Joint managing directors

Dr. Ernst Döring Chief chemist.

The printing of calendered Mipolam sheet was taken up by Schlieper and Baum in collaboration with Dynamit A.G., Troisdorf. Troisdorf supplied the Mipolam, which was printed by Schlieper and Baum and returned to Troisdorf. The printed Mipolam was sold by Dynamit A.G. through their sales organisation, Venditor, Dr. Fromm being in control of printed Mipolam sales.

In all, 400,000 meters run of 92-95 cm. wide Mipolam were printed by Schlieper and Baum in the years 1941-1943. Supplies for this civilian purpose were not permitted by the German Government, and such supplies as were forthcoming were unofficially engineered by Troisdorf. No more Mipolam became available after about April 1944. All accumulated stocks of printed Mipolam were burnt in the 1943 air attacks.

Only two small samples of printed Mipolam were seen during the visit (see Figs. 24 and 25). Both had been printed on a brown tinted Mipolam. One was the white check design already seen at Troisdorf (part 2); the other was a two colour cross design printed in red and yellow, much less effective than the other.

Essential points in printing of Mipolam.

The chief difficulty in printing Mipolam is to secure adequate adhesion of the ink, so that it does not drop off with wear or folding. This has been overcome by Schlieper and Baum by suitable ink compositions and technique of printing.

Ink composition.

The firms chemists working on the problem (Drs. Döring and Grassmäder) tried a range of lacquer basis dissolved in organic solvents as media for the colours, but found generally that the inks possessed poor adhesion; further, as it was necessary to do the printing at low temperatures on account of the low softening point of the Mipolam sheeting, difficulty was experienced with tackiness of the print through retention of solvent, even when volatile solvents were used. After-chlorinated polyvinyl chloride (I.G.'s Igelit PC) which was of interest because of its enhanced solubility, showed this defect.

The only material which has been found suitable as a binding material for the inks is the unchlorinated, low-soluble polyvinyl chloride (Igelit PCU) of the molecular weight normally employed for plastics work. Using this as binding material for the inks, claims are made of satisfactory adhesion with ability to operate the printing process free from interruption.

Polyvinyl chloride plasticiser is added to the composition in amount sufficient to plasticise the polymer present to the same degree as the Mipolam sheet being printed. This has the advantage of improving the resistance of the print to cold.

Initially, the ink compositions were made up with solvents based on cyclohexanone, but containing also more volatile solvents such as acetone and benzene. It was found in practice that these inks dried out too quickly, giving print of inferior adhesion. Finally, cyclohexanone alone has been used.

Formulae.

The only colours which have been so far employed are white, yellow and red. The formulae for the inks are as follows:-

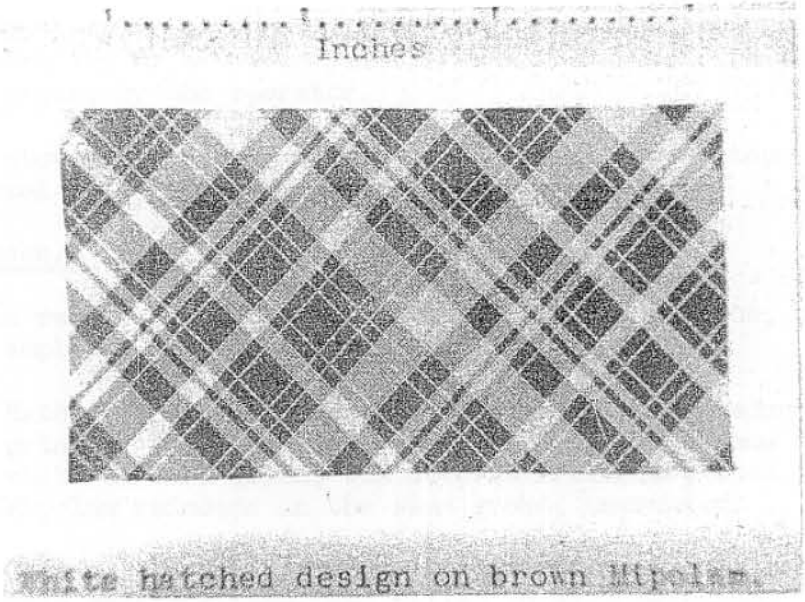


Fig. 24. Printed Mipolm, Schlieper & Baum.

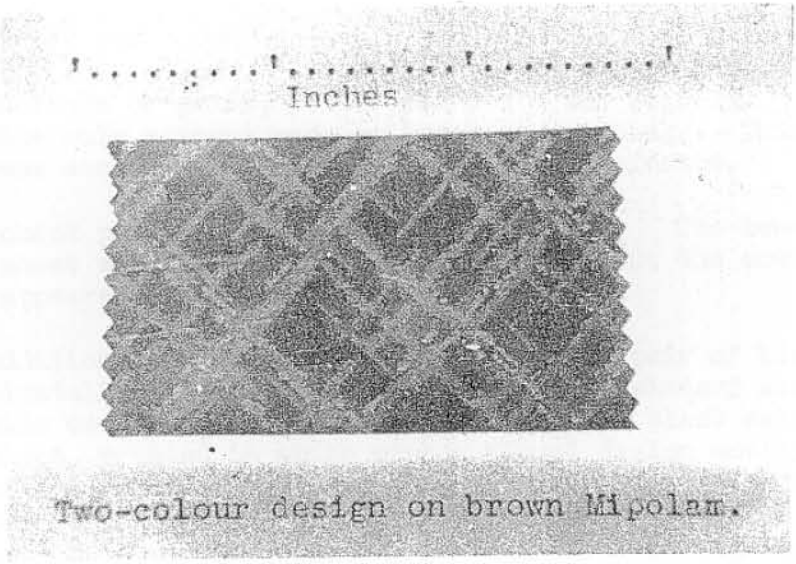


Fig. 25. Printed Mipolam, Schlieper & Baum.

The pattern is cut into the roll by these scribers, which are operated pantographically by a master point. This is moved over the design, drawn on paper, by the operator.

The above engraving processes are claimed by Schlieper and Baum to be normal in the preparation of printing rolls.

Designs seen.

Rolls were seen engraved with the following designs, which had all been employed in printing Mipolam.

(a) Hatched check design, originally seen at Troisdorf (white print on brown Mipolam, see Fig. 24). The same design, in white on dark green, was seen at Troisdorf, used to trim a Mipolam raincape in the same green, unprinted.

(b) Viennese pattern - dots about 3/16" diameter, spaced about 1". Dots were outlined, and filled in with hatching. No examples of print with this pattern seen.

(c) As (b) but the circles were filled in with punched dots. No examples of printed Mipolam seen with this design.

(d) Intertwined leaf design, outline only in dotted line; no filled areas. No examples of print seen.

(e) Cross two colour design - punched design. Two rolls, one for each colour. Printing done in one passage of the machine. Colours of print, yellow and red - see Fig. 25. This was the only attempt made at 2-colour printing. This material was seen at Troisdorf made up into a raincape.

The check printing appeared very effective. The two-colour printing sheet was not attractive as a design, but the actual printing appeared effective technically.

In addition to the above designs, we saw a pair of black-out curtains installed in the house of one of the Troisdorf staff. The curtains covered a large window, and were of black calendered Mipolam sheet, printed in white with a floral design mostly in dotted outline, with small dot-filled areas. The design and the appearance of the curtains were very effective. Although these curtains, which covered a space of perhaps ten feet high by twelve feet wide, had been installed for two or three years, they showed no signs of sag.

Printing details.

After leaving the rolls, the Mipolam passes up to the drying floor, and through the drying maze; it would appear to have a run of 60-70 feet before it is wound up. The rate of printing has reached 25-30 meters per minute; the limit of the printing speed is set by the tendency of the Mipolam to stretch under the increased stresses obtaining at the higher speeds. This leads to rucking in the wind-up roll. Improvements in stentering might lead to improvement in this respect.

The drying run is carried out normally without heat in the radiators and drying plate but on cold days, they may be warmed slightly.

Patent.

Schlieper and Baum have a patent covering the printing of Mipolam sheet using inks based on a solution of unchlorinated, low-soluble polyvinyl chloride containing plasticisers. Reference - D.R.P. 740112, application 24th April 1941; published 12th October 1943.

Erwin Wintgens. 1 Parkplatz strasse, Elberfeld.

Mr. & Mrs Wintgens own a tailoring factory in Elberfeld, and have had experience with Mipolam. They could produce 1000 raincapes per month if the material were available. The capes are made in the same way as those seen at Troisdorf. Seams are doubled and sewn and are not solutioned or overlaid. Heat or H.F. sealing is not used.

As other outlets for Mipolam sheet, the usual curtains, babies' panties, and umbrella coverings were mentioned. No new suggestions were made. Mr. Wintgens expressed a preference for Mipolam calendered on cloth on account of its greater strength; the novelty aspect of the unsupported film, however, was of attraction to Mrs Wintgens.

D. Cable masses from polyvinyl chloride.

Dynamit A. G., Troisdorf, near Siegburg, Rhine Province, and Krümmel, near Geesthacht, Hamburg

Interviewed :

(Troisdorf) Dr. R. Röhm , director in charge of Mipolam Department of the Plastics Section.

Dr. Raalf, Celluloid Laboratory.

(Krümmel) Dr. J.C.E.Neale, managing director.

Dr. Mielke, chemist in charge of the Plastics Section.

Whilst to foreign visitors to Germany the most interesting developments in application of polyvinyl chloride are probably those connected with the production of calendered soft Mipolam sheet, and the various uses of processed hard Mipolam (Luvitherm film, and chemically resistant plant linings and apparatus from Vinidur), yet to the Germans the use of plasticised polyvinyl chloride for extrusion as insulator over electric wires and cables must have been, and may still be of primary importance.

At least 28,000 tons of polyvinyl chloride were produced in Germany in 1944. Manufacture of soft Mipolam calendered sheet had by then been prohibited, and whilst the breakdown of the above production of polyvinvyl chloride has not yet been ascertained, it seems likely that a very considerable proportion must have gone to make various forms of wire covering.

Cable masses of plasticised polyvinyl chloride are appreciated in Germany to have the same advantages and disadvantages as are recognised outside that country. The high resistance to atmospheric oxidation is an advantage, whilst the difficulty of combining satisfactory flexibility and cold resistance with high resistivity is a disadvantage.

All polyvinyl chloride manufactured by I.G. is prepared by the polymerisation of vinyl chloride stirred to form a stable emulsion in an aqueous medium containing soapy materials, (e.g. Mersapol, $C_nH_{2n+1}SO_3Na$) which stabilise the disperse phase, and a water soluble oxygen polymerisation catalyst, such as potassium persulphate. The polymerisation has been recognised by the I.G. chemists for some years to proceed through the vinyl chloride dissolved in the aqueous phase. The solid particles in the polymer dispersion obtained adsorb strongly both

dispersing agent and catalyst residues, and the processes involved in isolating the solid polymer do little or nothing to desorb them. As a consequence, I.G. polyvinyl chloride has a high ash, 1.5 - 2%. The presence of this ionised material is used to explain the high water absorption and low resistivity of Igelit PCU.

Wacker's of Burghausen also make a polyvinyl chloride (Vinnol) by polymerising a comparatively coarse (unstable) suspension of vinyl chloride droplets in a dilute aqueous solution of polyvinyl alcohol, which stabilises the suspension so long as stirring goes on. The polymerisation catalyst is benzoyl peroxide, dissolved in the vinyl chloride, and polymerisation proceeds on the organic phase, to give a granular product.

As has already been reported (C.I.O.S. Report XXIX, 62, p.51) the water absorption of Vinnol is much less than that of Igelit PCU, which is consistent with the much smaller adsorbate, but figures obtained at Troisdorf (see Appendix 1) show that the specific resistivity of a plasticised composition made from Vinnol is no better than that of a composition based on Igelit PCU.

In the course of discussions with German chemists no indication has been obtained that they had any information which would bear on the following a priori possible causes of poor resistivity in PVC cable masses --

Self-ionisation of polyvinyl chloride, leading to conductivity by solution of the ions in plasticiser or adsorbed water.

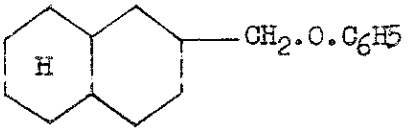
Conductivity due to hydrogen chloride formed by decomposition of PVC during processing.

Hydrogen chloride from dehydrochlorination during polymerisation (Staudinger and Schneiders, Ann 541, 151-95 (1939): this work seemed to have been generally forgotten).

New plasticisers. Plastomoll TV had been stated at Ludwigshafen to be outstanding in electrical properties when used as plasticiser for polyvinyl chloride. Plastomoll TV is an (average) C_7 alcohol ester of thiodibutyric acid.

$$(C_7H_{15}.O.CO.CH_2CH_2CH_2)_2S.$$

Similar claims were made by Troisdorf for Teolan P, the phenyl ether of beta-hydroxy methyl tetrahydronaphthalene -



As is shown by the following figures for specific resistance obtained by Troisdorf, the superiority of these plasticisers over normal plasticisers is limited, and does not bring cable masses made from them into the rubber insulation class. Whilst Teolan P gives poor cold resistance, Plastomoll TV is good, even with the comparatively small amount of this plasticiser used in the composition.

Comparison of properties of plasticised polyvinyl chloride cable masses.

Composition	Specific resistance at °C ohms/cm.		Cold Resistance (fails impact test at °C.)
	20°	80°	
70 Igelit PCU (grade K). 15 Palatinol HS (C_{6-7} phthalates). 15 Palatinol F (C_{7-9} phthalates)	2.1×10^{12}	4.7×10^{9}	-5° to -15°
79 PCU 21 Plastomoll TV	3.8×10^{12}	1.8×10^{9}	-5° to -20°
67 PCU 33 Teolan P	5.5×10^{13}	5.6×10^{10}	+15 to + 10°

Production of cable mass at Troisdorf.

Some differences exist between the procedure for cable masses and that for calendered sheet mass. Cable mass is not actually in production The plant was inspected and information obtained from Drs Röhm and Raalf.

Stabilisation of polyvinyl chloride. Stabiliser is added to polyvinyl chloride for cable masses, in contradistinction to calendered soft Mipolam. The stabiliser at present used is alpha phenyl indole, 0.5%.

Premixing. The polymer-plasticiser mixture is premixed in Werner-Pfleiderer mixers (400 liter capacity) as for calendering.

Rolling. The set of rolls used for mixing cable masses consists of 2 normal Troisdorf Mipolam rolls (1100 x 400 mm.) and 3 large rolls (2000 x 750 mm.). The latter are celluloid rolls adapted for this purpose. They have no friction, and revolve at about 6 r.p.m. The set of rolls is driven by a 110 KW motor through a countershaft in the floor.

The large rolls take a charge of 150 Kg of composition and the charge is worked for 30 minutes at 160 - 170°. The crepe is very thick, about 2 cms. in a specimen seen.

After mixing, the crepe is cut off, and filtered to remove dirt and lumps of unplasticised polymer, which can mar or weaken the extruded cable covering.

Filtering is carried out in hydraulically operated vertical celluloid strainers, the cylinders of which are jacketed for steam to give a temperature of 160°. The filters are circles of woven iron wire, about 1 mm. diameter, with spaces about 1 - 1½ mm. square. These filters are supported at the bottoms of the cylinders by filter plates bored with many holes , those seen being about 5 mm. diameter. The filtered Mipolam passes through and is formed by them into cords of about this diameter. The cylinders were approximately 12" diameter by 30" high.

A rolled-up "dolly" of Mipolam from the mixing rolls is placed in the cylinder, and compressed hydraulically by the piston. The internal pressure was not exactly known, but was stated to be several hundred atmospheres.

The filtered Mipolam cords passing through the filter plate, stated to be about 5 mm. diameter, are cut into lengths about 30 - 40 cm. and sold as such for cable covering.

For production of the so-called "endless" cord, the filtered material is re-extruded and wound off on the fiber drums. This re-extrusion is expensive. The product has however the attraction to the cable coverer of requiring less attention when being used with a screw extruder for cable covering. The drum of cord is suspended, on a free axle running through its central bole, near the hopper of the extrusion machine, and the end of the cord led into the machine. The pull of the extruder screw is sufficient automatically to reel off the

G. Gramophone records based on polyvinyl chloride.

Deutsche Grammophon G.m.b. H.

Podbielski Strasse, Hannover.

Interviewed: Herr Haertel, works director
Herr Schmidt, works engineer.

The works of this company are in a comparatively undamaged condition and at the time of the visit (22.9.45) were operating under orders of the Military Governor producing sound records of or for the Belsen trial.

The object in visiting this factory was to check information received in London that polyvinyl chloride was being used in Germany for the production of gramophone records. Herr Haertel denied any knowledge of this development but said that Mowilith (polyvinyl acetate) and Troschell (a shellac substitute based on aldol) had been employed.

The main constituent of war time gramophone records in Germany was ground scrap records which were plasticised with Mowilith and a plasticiser FXH supplied by I.G.Farben, Ludwigshafen. The composition of this plasticiser was not known to Herr Haertel nor was the exact grade of Mowilith used. All that was known was that the Mowilith was supplied by I.G.Farben, Höchst.

The composition of the mix used was as follows :--

500 kgs ground scrap records
3 kgs Mowilith
8 kgs FXH or natural copal if available

This was compounded in the normal manner on mixing rolls and finally pressed into finished records. When natural shellac was freely available the preferred composition was --

30% shellac
30% slate dust
18% silica
22% quartz meal.

An inspection of the process in operation was made but there did not appear to be any novel features.

The scrap records were ground in a No. 4 Progress Mill (Miracle type) made by Fellner and Ziegler, Frankfurt-on-Main West. This mill has two sets of fixed teeth on the hinged front section and three sets on the back. There are four hammer arms each with a swinging hammer head with three striking surfaces. These heads are forged from

Cr.- Ni steel and have approximately 200 hours working life. When the heads fail it is usually the outer grinder which fails. When this happens the remaining portion of the striker is fitted in a holder and used with only two striking pieces. The ring mesh fitted is metal perforated with 2 mm holes.

These Progress grinders are fitted with roller bearings and have a maximum operating speed of 1700 r.p.m. For grinding scraps the speed is 1200 r.p.m. The mill in use at the Deutsche Grammophon works has been running successfully since 1926. Previously a pin mill was used but was unsatisfactory because it clogged up.

The ground material, mixed with the plasticisers is mixed on differential mixing rolls of conventional type (size : length 1200 mm, diameter, 400 mm.) The rolls speeds and temperatures are -

Front roll	speed 22 r.p.m.	Temperature	107 °C
Back roll	" 24 r.p.m.	"	150°C

A 25 kg batch of the material is rolled in the normal manner. Material which does not flux during the first passage through the rolls is caught on a sliding tray and picked up by cutting off a portion of the plastic mass and using this to pick up the loose dust on the tray. The rolling time for a material using ground scrap is 6 minutes and for a composition of the preferred type containing shellac the time of rolling is 14 minutes.

When rolling is complete, a point which is apparently only judged by time and the skill of the operator, the sheet is cut off and passed through even speed sheeting rolls. Immediately following these rolls are four marking blades set at right angles to each other and six marking wheels. These mark the sheet off into rectangles $6\frac{1}{2}$ x 5". When the sheet is cool it is broken by hand along the marked lines and the rectangular pieces are ready for final processing.

This is done by preheating the pieces on a hot plate heated by steam as $8\frac{1}{2}$ atü. Three pieces are used for a 12" record. The preheated material is moulded in a press heated with steam as $8\frac{1}{2}$ atü and under a pressure of 85-90 kg/cm^2 acter cooling the finished record is removed from the press.

Troschell, the shellac substitute based on aldol, made by I.G. Ludwigshafen and sold by Venditor, Troisdorf was satisfactory in use but was unobtainable during the war.

No samples of records made from material containing Mowilith were available. Those being made were produced from ground scrap with a small proportion of natural shellac.

Appendix 1

Translation of letter from D.A.G., Troisdorf, to Colourist Section, I.G., Ludwigshafen, 14.3.41.

Vinnol HH.

We have tested the Vinnol HH of Dr. Alexander Wacker A.G. submitted to us in respect of its suitability for the production of plasticised masses.

Since we had shown in a preliminary experiment that the material colours much on the hot rolls, we added stabiliser DBG to the mass.

The experiment was -

65 parts Vinnol HH
35 " Tricresyl phosphate
2 " Stabiliser DBG (Diisobutylphenyl glycidyl ether)

The mass was worked on the rolls at 170 - 175°. It could readily be rolled, but became reddish-brown in colour. The crepe was as usual pressed into sheets.

For comparison, Igelit PCU grade K, batch 1646 was worked up according to the same recipe, but without stabiliser. The roll temperature was 160°. The mechanical and electrical values obtained are set out together in the accompanying table. From it one observes that the mass with Vinnol possesses higher tensile strength, a higher Vicat value, rather better cold stability, and better water resistance. In the matter of extension at break, stiffness, and electrical values the masses are equivalent. The improvement in tensile strength, Vicat tests, and water resistance obtained with Vinnol HH is quite considerable.

The introduction of Vinnol HH in place of PCU would be a considerable advance.

Comparison of Vinnol HH with Igelit PCU

Experiment number	K 2527		K 2528		
Recipe	65 Vinnol HH (k=80-90) 35 C II B 2 DBG		65 PCU (k=75) 35 C II B		
	Direct	Aged	Direct	Aged	
Tensile strength -					
Along rolling line	355	284	244	218	kg/cm^2
Across " "	336	295	256	228	"
Extension at break -					
Along	262	292	293	275	"
	238	270	278	267	"
Stiffness	7.5	3.9	7.6	4.2	cmkg/cm^2
Heat stability,					
Vicat type	125°	147°	92°	118°	
Cold impact test	0°	+5°	+5°	+5°	
Spec. resistance,					
direct	1.74 x 10^{11}		1.09 x 10^{11}		ohm x cm.
24 hr. in water	2.79 x 10^{11}		1.42 x 10^{11}		"
Surface resistance,					
direct	3 000 000		500 000		M ohm
24 hr. in water	750 000		190 000		"
Intern. res. direct	3 000 000		3 000 000		"
24 hr. in water	1 500 000		1 500 000		"
Water take up at 20°	0.77		3.92		%
" " 70°	12.3		27.2		%

Appendix 2.

0.12 mm. transparent soft Mipolam sheet for raincapes.

Formula PCU 5280

71% Igelit PCU grade G (polyvinyl chloride)
29% Plastomoll KF (triethylene glycol ester of fore-run synthetic fatty acids)

100%

Tinting for 100 kg of mass.

2 g Vulkanechtblau GCF paste (Indanthrene Blue GG (I.G.))
0.73 g Vulkanechtviolett 3 BF paste

Manufacturing procedure.

The raw materials, Igelit PCU, Plastomoll KF, and colour, are mixed or gelatinised in the usual mixing machines (stirred apparatus), or in Werner-Pfleiderer mixers at a temperature of 130-150°. The mixture is then thoroughly plasticised to complete homogeneity on rolls at 160-170°. The rolls are as follows -

Length of rolls	1000 mm.
Width of rolls	400 mm.
Speed	15 r.p.m.
Friction	1:1.3
Size of motor	40 KW
Power usage	25-30 KW

On an average, the rolling time amounts to 30-40 minutes for a charge per roll of 15 kg. In general, three rolls in series are used simultaneously. The material is taken in pieces from the rolls and fed between the upper and middle bowls of a three-bowl calender. The calender has the following dimensions -

Length of bowls	1300 mm.
Width of bowls	600 mm.
Speed	3.5 - 14 r.p.m.
Friction	none
Temperature -	
upper bowl	170 °C.
middle bowl	160 °C.
lower bowl	155 °C.
Motor size	22-110 KW
Power usage	60 KW

The soft Mipolam sheet of thickness 0.12 mm. is processed at a wind-off speed of 7 meters per minute. The second bowl-nip is adjusted for the exact thickness by two regulating motors. As it is wound off the sheet passes first over a chromium-plated cooling roll lying behind the calender, then over a stenter (Breithalter) and through a trimming machine with incorporated talcer, and is finally wound up on a pulp-board spool. The weight of a roll is about 30 kg.

Troisdorf, 29.9.1945.
Dr. Rö°/Kk