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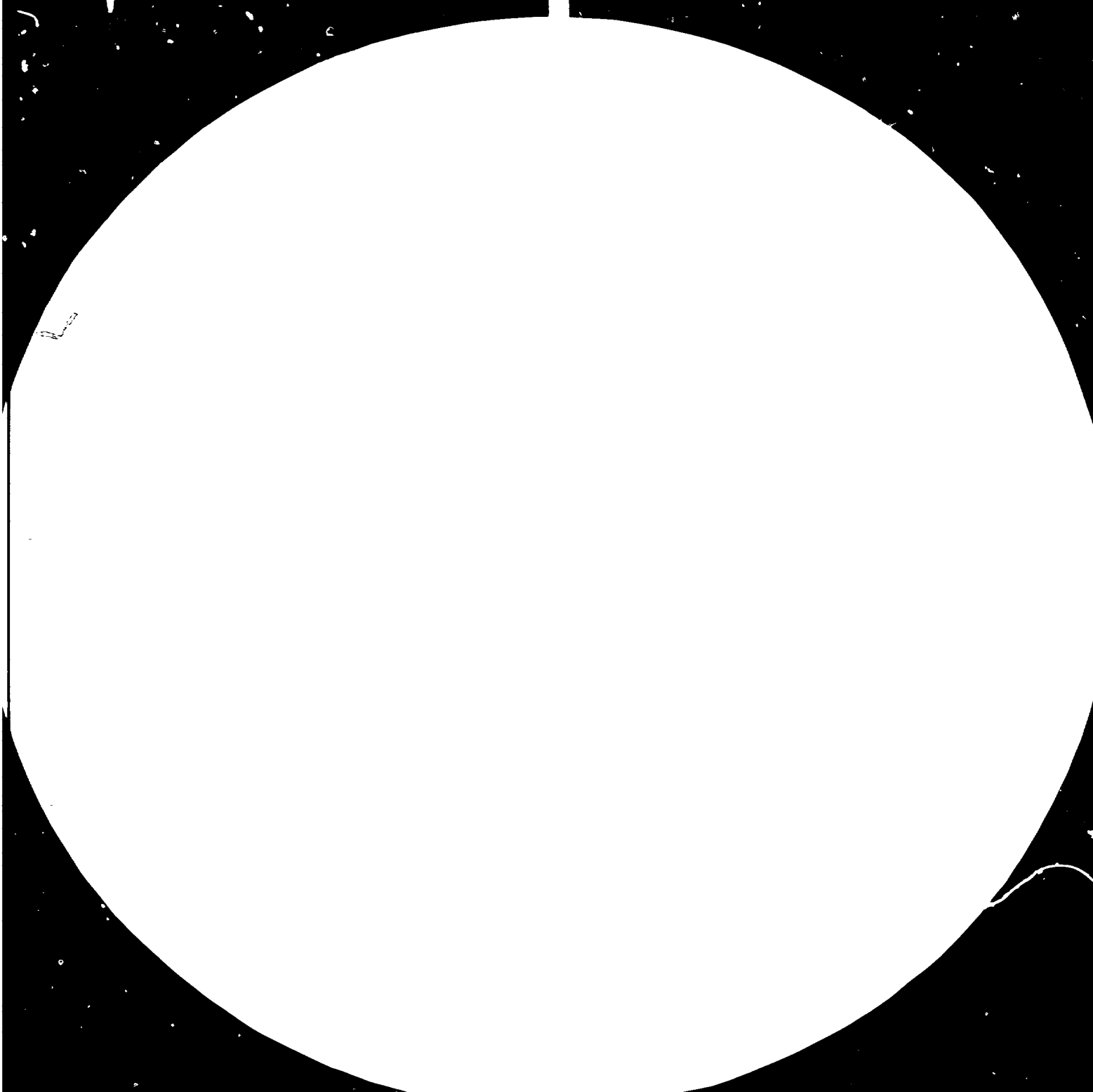

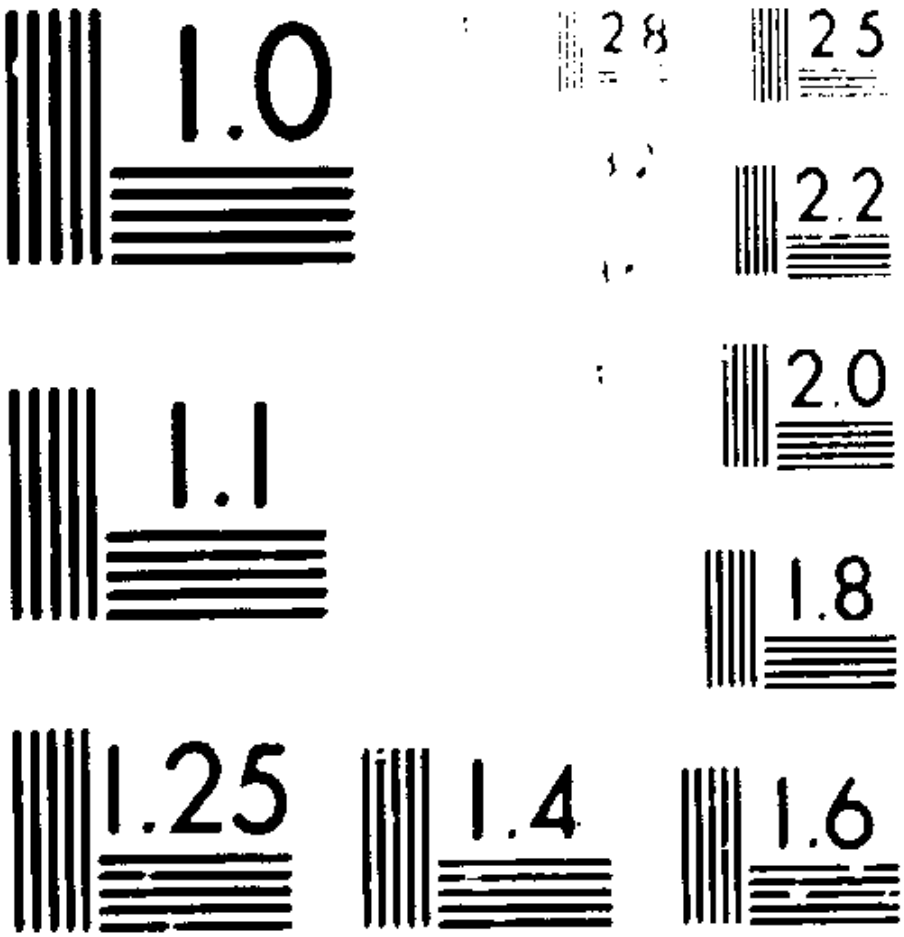
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A BRIEF REPORT ABOUT THE PRESENT TECHNICAL SITUATION OF PRINTING SYNTHETIC FIBRES AND THE MOST IMPORTANT BLEND POLYESTER/CELLULOSIC.

R. SCHULZ

Introduction

Let us start with a few words about the history of printing. We imagine that the first step of printing is that natives painted their body. The next step perhaps to paint woven fabrics with various colours like in Egypt. The next techniques are developed in South and Eastern Asia. With ropes or wax the fabric was made resistant against the following dye-bath. It was called Bandhana and Batik technique.

In Europe was the first industrial step the hand block printing. Wooden blocks covered by patterns, either engraved in the wood or setting in metalleous paths. You must print each of these small blocks and each colour separately and this is not suitable for a large production.

In respect of this point a semi automatical machine was constructed at 1834 from Perrot. This machine used up to six large hand blocks and the fabric moved the distance which belongs to the width of the block. It looks like automatical stamping. The first real industrial machine which is used till our time is the roller printing system. The first of them was designed by Bell in Lancashire and they became rapidly so perfect that when you except improvements in details or reasons of better materials were founded the same system is existing till this days.

At the modern roller machine the fabric runs continuously up to speed of 12000 m/h. The system is as follows: Engraved copper rollers (the diameter is approx. 20 cm) are arranged around iron pressure cylinder called Presseur. Around this pressure cylinder was put in layers a soft fabric so that the rollers have a smooth pressure. Around the pressure cylinder is running an endless rubber conveyor band. Between this rubber band and the roller is running a cotton fabric which prevents hurtings of rollers and band and which also picks up the additional printing paste. This cotton fabric must be washed off after each using.

The application of the printing paste is that the roller is running in the print paste and with sharp blade the surplus is scraped off the polished surface. So the paste is only in the engraved areas of the roller.

During the printing the fabric is squeezed between the rollers and the pressure cylinder and the fabric picks up the print paste remained in the engraves. So you can print up to 12 colours in one process.

The preparation of engraving the copper rollers is a photographical method. the parts of the patterns which should be not engraved are covered with a liquer which prevents that the copper will be not destroyed in the following acid bath.

So the conclusion that roller printing is from view of engraving very expensive and the rentability is only quite good if there are high productions in the same pattern.

Screen printing in original form is based on a technique that a very thin gauze is stretched very strong in all directions over a metallic frame. Mostly the gauze is PE or PA. With a light sensitive lac the gauze is impregnated and after drying the photographic made foil is pressed on this so prepared screen and it is lightened, where the light is coming to the sensitive lac it becomes hard, where not it is water soluble. In the open areas the printing paste can penetrate to the fabric.

The system is that the fabric is glued on a table and the pattern repeat is done by the printer. It is called "Table printing".

The next step in flat screen printing was developed by Co. J. Zimmer in Klagenfurt/Austria. The system is that the screens stable and the fabric moves to each pattern repeat from one to the next. This system is working with a magnetic roller which is pressing the print paste through tho open blotches on the fabric. The maximum speed is up to 340 - 400 m/h. This kind of equipment allows with relatively cheap creens that you can go easily in the mode business.

The last development in printing is the rotary screen printing. It is a printing method in which the print paste is applied to the fabric with squeezes (Storck) or magnetical (Zimmer) via seamless cylinder made metallic foil (Nickel).

The print paste is pumped into this cylinder and hold at the same level by automatical level controllers. The advantage of this type of printing machines is that the screen costs are much lower than rollers and it belongs very intensively to the world market price of copper and the higher the raising of the copper price the lower are the costs for the screens.

The absolutely last development in printing is the so called "Transfer printing". The transfer print process is based that a special prepared carrier material (normally paper) is printed similar like wall paper printing. In this case you can only use in the present situation disperse dyes which are only suitable for PE and with reservations for PAM in pale shaedes.For natural fibres was developed a system but it is similar tc the normal printing. Coming back to synthetic fibres the system is relatively simple. Dyestuffs with a low sublimation fastness are printed on the paper and under heat conditions of approx. 200 - 220^{0} this paper is pressed against the fabric. The dyestuff shows a migration because it is going to a phase of sublimation, it means to go from the solid form to the gas form.

The advantages of transfer printing are a simple working process, nearly complete fixation, no after treatment, difficult pattern with fine outlinings are optimal like paper printing. No water or air pullution.

The most essential requirement of printing is the thickening. In all kind of dyeclasses without pigments it is nearly the same recipe. Dyestuff, an agent for better solving like urea, thiodiglycol then water, thickener based on alginates, gums, locust been deriwats, chemicals for dye fixing and antifoarming agents.

Choice of thickening

In printing dyes are applied from a thickening medium. Thickenings differs in their properties and in their ability to hold the dye within the area to be printed (sharpness) as well as in their consistency and chemical stability. As their compatibility with different dye groups varies and the differences in their reaction to steam and dry heat, there is no thickener suitable for universal application.

The methods of application are:

Direct printing is in most cases carried out on white goods.

Overprinting means direct print on a pale ground to give heavy shades. The dyed ground is not destroyed.

The Classic Discharge printing with exeption of the new method of PE discharge we will discuss later.

Fully fixed and washed dyeings are printed that the dye is locally destroyed by reducing agents in the print paste and the original color of the substrate is shown ; this is called a white discharge. If dyes are added to the discharge paste which are not reducible, the discharge area becomes coloured and is called coloured discharge.

Fixation of the prints

The fixation method can be divided into two main types:

one-stage methods with dry fixation:

1) steaming
2) short steaming
3) thermofixation (hot air)

With these methods of application all the chemicals are already present in the print paste.

two-stage methods with wet fixation:

1) alkaline-shock (fixation in the development bath)
2) cold pad-batch method

With these methods the chemicals used for fixation are applied by an additional process.

In principle steaming is the only one of the above methods that can be used for all types of dyes. In the steamer water vapour is condensed on the surface of the fabric to give the moisture, needed to swell the fibre and thickening and to dissolve the dye. So can the dye have a physical or chemical reaction with the substrate.

Short steaming by high temperature

High temperature steaming with superheated 100% steam at 160 - 185°C has more and more taken place of the hot-air fixation. Especially it is used for the fixation of disperse dyes on Polyester and blends PE/cellulosic. The recently development loop steamers are qualified for continuous working, whereby the textile material is transported through the equipment without tension, because it is hanging in loops. It is the best method for knitted fabrics.

Hot air fixation

This method will be applied if no steamer is existing in the factory or if setting of the synthetic material and fixing of the prints has to be done in one stage. The dry heat fixation needs only very short time, depending on the material and the type of dyes. The results are often not as good as those obtainable by high temperature steaming.

Wet fixation

The dye will be fixed by helps of chemicals applied in the developing bath. The fixation will take place according to the temperature of the bath immediately, if the temperature is high enough or it will take hours, so we have to store the goods. The first method saves time, the second saves the costs of the heating times.

Washing-off of printed material

After the dye has been fixed on the fabric each part of unfixed dye, thickening and chemicals must be completly washed off.
The washing-off process is important for brilliance of shade and good fastness. Normally the goods are rinsed first in cold water so that most of the unfixed dye and thickening may be dissolved and removed. To prevent staining of the white ground the rinsing bath must be frequently renewed. When the rinsing water is clear the goods are washed in warm or hot water, depending on the type of dye and fabric.

Now I am trying to explain the different classes of dyes which are used especially for synthetic fibres and their blends. The most popular kind of printing is in the moment the

Pigment printing

The reasons are very simple. It is relatively cheap in after treatment because it needs no washing-off process. The pigment print fits theoretically for all types of fibres but in practice it is limited by fastness and handling reasons. With handling I will say that especially in heavy shades the printed material is not so soft as wanted . The group of the pigment dyes consists from coloured anorganic pigments like ironoxyd to organic pigments like vats or phthalocyanines or on the white section Titandioxyd. Practically a wide range of pigments have a good fastness against clorine,oxydation and gas fumes. The light fastness is in the most cases very good.

The most important chemical in pigment printing system is the binding system. The pigment dyes have no adhesive to the fibre so they must gluten on the fabric. There is a number of different syntetics like polycondensates, acrylates and so on. Each of this bindings has an advantage. One of them good light fastness, the other one needs only a short condensation time, third shows a good rubbing fastness and so on. So the decision what type of binding system a factory uses depends to the qualities of fabrics and the fastness requirements.

The second point why pigment printing system has a difference to all other systems is that there is used an emulsion thickener based on water, white spirit and an emulsifier. In principal there are existing two sorts of emulsions. It is "water in oil" and "oil in water". As I know, is only used the oil in water emulsion because water is the outward phase and the washing-off properties of screens and the other equipments are no problems. In the last years there were started many trials of the most important producers of binding systems to substitute the white spirit emulsion by synthetic thickeners. The most important material on which it based is a type of acrylic acid like Maleinacidanhydrid. This types build up macropolymere acids with a very high viscosity. The reason for this development is that the governement in many (especially European) countries dont allow further the danger of explosivity and the pollution of the white spirit to the air.

With the synthetic thickeners, perhaps, we will get a financial problem. The acrylic derivates are synthesiced from oil. The price increasing of oil products prevents in my opinion a quicker development for these, lets say pollution kindly method of this new thickener generation.

Printing on polyester

The disperse dyes are the dyes mainly used on polyester. A wide range of these class of dyes has been developed, different in their properties,concerning lightfastness, sublimation-fastness possibility of fixation or better suitable for several type of fibres.

Disperse dyes exists mostly in two trade forms as granulets powders or as liquids. In the printing industrie there are only used the liquid brands, because if you handle this dyes as prescribed you have no stipping problems.
For printing the polyester fabric this should prepared by presetting and scouring with a nonionic detergent.

The pretreated polyester fabric is now printed with disperse dyes, it is possible to use a classic thickening like locust bean flour derivates or to use half emulsion thickening.
A standard formulation for paste with classic thickening is: disperse dye, thickening, milde oxidizing agent, anti foam agent, water.
The reaction of the paste must be neutral or slight acid, as many disperse dyes are sensitive against alkaline reaction
If emulsion thickening should be used prepare the stock thickening by adding an emulsifier and auxiliary like Luprintan ATP, BASF which improves depth of shade and shortenes fixation time.

Fixation

The fixation on polyester is more expensive then on the other synthetic fibres because higher temperature is needed.
Best results in fixing gives the pressure steaming process

20 minutes, 1,5 atü, 120 - 125 ^{o}C

The advantage of this proceed is:

wide range of colours because lower claims on sublimation fastness,
No injuring of the handle as steaming takes place at a relative low temperature,
In most cases better yield od the dyestuff,

Disadvantage: discontinuous working!

Fixation at high temperature steaming:

165 - 170^{o}C 10 - 15 minutes

Results are not as good as with pressure steaming.
Advantage is continuous working.

Fixation with hot air (thermofixation)

It takes place at

200 - 210°C, 30 - 60 seconds.

Only disperse dyes with high sublimation fastness can be used! Advantage are the short time for fixation and the continuous work. The handle of the fabric will be influenced by the tension and the high temperature. Some thickeners , such as gums or locus-bean-flour-derivates get hard through this process and cannot be washed-off afterwards, so the result is a stifffeeling of the material and a low rubbing fastness

Aftertreating

The goods should cold rinsed and soaped with nonionic detergent at 80 - 90°C for 10 minutes. It is always necessary to aftertreat PE with a reducing agent like Hydrosulfit at a temperature between 70 and 80°C. The rest of the unfixed dyestuff will be destroyed and you get the optimum of fastnesses.

Discharge printing of PE

In the last few years there was developed a new class of disperse dyes by ICI which can be destroyed by a strong alkaline print paste without reduction agent.

The basic requirement is that the pretreated fabric will be padded on a foulard with Dispersol-PC dyestuff, auxiliaries, antifoaming agent and a little quantity of thickener. The drying temperature after this process should not be higher than 80°C.

Then it will be printed with alkaline resistent disperse dyes and 50 g/kg Sodium lye 38° Be.

In the following steaming process at HT conditions 165° - 180° the alkaline destroys the ground shade and the disperse dyes in printed pattern and ground will be fixed together.

The washing-off process afterwards is the same like conventional PE direct printing.

Printing of polyester/cellulosic blends

The most important blend is world wide the mixture mentioned above. It is used for shirts, blouses, summerwear, bedswear and many other employments. But it is relativly difficult to print this blend. Actually there are only two types of dyestuff classes which are used. The first is the pigment we mentioned before. The second is a mixture of two dyestuff classes, the disperse dyes in a combination with reactive dyes. The advantages of pigments are the easy handling, the easy printing and cheapness. The disadvantages are relatively low rubbing fastness, less air permeability and lower washing fastness versus the mixture dyes. The disadvantage of the mixture is the washing-off process because the unfixed disperse dye part of the mixed dyestuff is very resistant in the cellulosic fibre. So especially in heavy shades with white grounds you have very often problems to clean the fabric to the original ground shade. It needs a lot of water and patience for this process and the result cannot be guaranted in all cases. The process is also very expensive.

For printing with the disperse/reactive dyestuffs you need as thickener an alginate. The reason is that the reactive dye has a chemical affinity to the cellulosic fibre and similar molecular groups are in the classic thickeners. So it happens that the dyestuff has a reaction with the thickener and is lost for the fabric. The fixing conditions are normally HT steaming 170 -180°C, 10 to 15 minutes.

The washing-off recommendationes are to do it in continous washing boxes

rinsing cold
rinsing cold with a nonionic auxiliary
washing-off at 50°C with auxiliary
soaping at 95°C with auxiliary
rinsing cold

An other fixing method is the thermo fixing method mostly done on a stanter. Conditions are 200°C, 60 to 90 seconds.

Printing on Polyamid

The pretreatment of the PA-material has to be done carefully especially the heat setting or stabilising. For soaping use an anionic detergent and soda ash at 60 - 80°C.

The setting may be done with

	hot air	Rilsan 150°
		Perlon 185 - 200°C
		Nylon 210 - 220°C
or	steam	20 - 30 min. 120 - 125°C
or	hot water	45 min. approx. 130°C
	bleaching	
	optical brightening	

Polaymid may be printed with the following dyestuffs:

selected acid - d.
metallic compex-d.
disperse-d.
selected direct-d.
reactive-d. for PA
pigments

For printing on the hydrophobe polyamid fibre the choice of the thickening is of great importance. Best qualified are thickenings with high solid contents, derivates of the locust-bean-flour, cristal gums, various gums in mixture with Alginate.

The acid dyes are the most important both for the wide range of colours and their brilliance. The difficulties known as "blocking effect" which occur, when dyeing PA do not interfere with printing. The wet fastnesses of acid dyestuffs are moderate up to good, so we should use only selected dyes.
An aftertreatment with an auxiliary such as

Cibatex PA, Mesitol Erional NWS

sometimes increase the wet fastness.
In the following let me show you a common formulation of a print-paste which is used for acid dyes or metallic complex dyes on PA:

dyestuff, Glycerin A (solvent for dyes), urea, water, thickening, ammonium sulphate.

Brilliance and building-up of the acid dyestuffs is very good also the lightfastness. They may be used even for dark shades when water and washing fastness claims are moderate.
Better results in this respect you get by using the metallic-complex dyes and by the reactive dyes, selecting only those which are suitable for polyamid.
Reactivedyes on Polyamid are used whenever good wet fastnesses are demanded. As disadvantage must be mentioned that the shades are duller and the print paste costs are much higher.
As thickening is used a high-or medium viscosity alginate.

Fixation takes place by steaming 10 - 15 minutes, 102°C, in a star or contonous steamer.

Aftertreatment consists in rinsing, soaping with a anionic detergent at 80 - 90°C for about 5 minutes. Rests of unfixed dyestuff must be removed thoroughly, then follows hot and cold rinsing. The hot soaping is necessary to avoid staining of the unprinted ground in a latter bath and further to obtain the best wet fastnesses.

Disperse dyes serve to print on polyamid big areas with pale shades which have to show even good results. Levelness in pale shades is difficult to get with acid dyes.
The fastnesses of disperse dyes on PA are moderate up to satisfactory.

Fixation after printing and drying may be done by
steaming for 30 minutes at 102°C, 0,5 atü
or hot air for 1 minute, 190 - 200°C.
Only disperse dyes with high sublimation fastness can be used.

Aftertreatment consists in rinsing and slight soaping at about 40°C and final rinsing.
There also exists a small group of direct dyes which have similar chemical constructions like the acid dyes. They are suitable for printing and they shows good light and water fastness. This selected group of dyes is relatively cheap and so very economical if you need cheap recipes. Sometimes you can combine them with acid dyes.

Pigment dyes on Polyamide

Pigment dyes can be used also on PA like on the other fibres. It is the cheapest way because aftertreatment is only a fixation process. Mostly it is used for cheap clothes and womens underwear.

There is existing also a special kind of modified PAM called Quiana. This type is printed with selected disperse dyes in the same way like PE.

Discharge printing of PAM

In some cases it is impossible to print patterns by the direct method especially when a big share of the pattern is the ground shade.

The way to produce this printings is briefly the following: The PAM good will be dyed normally on the winch or beam with selected dischargable acid dyes. The follows a normal printing process either with selected acid dyes which are not dischargeable or with selected vat dyes. In both cases is reducing agent necessary, aprox. 200 g/kg Decrolin (BASF), it is CI reducing agent no. 6.

During the steaming process the reducing agent destroys the ground shade and the discharge resistant dyes are fixed on the PAM fibre. By this printing method the steaming process must be handeld very carefully, there should not be air and only a low moisture in the steamer. If air and moisture is in the steamer the reducing agent will be destroyed before it destroys the ground shade and the result is not satisfied, let us say very bad. You also can have white borders around the printed pattern.

Printing on polyacrilic fibre

Polyacrilic fibres differ in their technical and colouristic properties according to the number and kind of unsaturated groups with different affinity against colours. If the share of copolymeres does not surmount 15% we are speaking from polyacrilic fibre and the slight differences in technical respect and colour depth on the various types can be neglected. If the share of copolymeres surmounts 15% we are speaking from "modacrilic fibres", they take up colours more easily .

Pretreatment: For printing the material must be prepared by rinsing
washing-off with nonionic detergent, pH 5-6
bleaching for highest white and
heat setting (stabilising).

Printing: Suitable are:
cationic dyestuffs
disperse dyestuffs

The cationic dyestuffs are most important as they show very good affinity to the polyacrilic fibre.
Contrary to their properties on other fibres like cellulosic the cationic dyes have very good fastnesses on polyacrilic and extraordinary brilliance. Due to its light-and weather fastness PAC is used for curtains, furnishings, sunblinds and due to its good handle and skin feeling, which is similar to that of wool textiles, it is used frequently for ladies wear and for knitted textiles. These applications open a wide field for the printer.

The printing paste

Very usefull is an auxiliary named "Glyecin PFD" (BASF which accelerates the fixation and provides much better colour yield. It is said to be an organic liquid with nitrilo-groups and should be incorporated into the paste. The thickening used for cationic dyes should not be reducing or alkaline. Recommended are derivates of locust-bean-flour or burned starch, in practice they unse mixtures of these thickenings with gums and similar products. Emulsion thickening is not used.

Fixation: the dryed prints are steamed in a star steamer

20 - 30 minutes, 102°C, 0,2 atü

The polyacrilic fibre is very sensitive to stretching or extending when treated with heat , folds, plaits and wrinkles are fixed permanantly, so the steaming process has to be carried out very carefully.

After steaming follows the aftertreatment:

rinsing with cold water

washing with nonionic detergent, temperature 50°C pH = 5 - 6

washing at 70°C,

rinsing

I even want to mention another method to fix cationic dyes on PAC, so the results are not as satisfying.

Fixation may be done in a stenter with hot air of 140 - 160°C during 45 - 60 seconds. The printing paste has to be adapted for this process by adding urea and other auxiliaries to swell the fibre.

Disperse dyes: They are used on PAC when big areas in pale shades have to be printed, as they give much better equalness. The lightfastness is only satisfactory, the wetfastness is good.

The prints are

steamed 20 - 30 minutes, 102°C, 0,2 atü

then follows rinsing, soaping and rinsing as yet described.

The discharge printing of PAC is not very popular because you need stannous chloride and by this method you will get a lot of troubles in the steamer.