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Characterization of pigments in coating formulations for high-end ink-jet papers

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Abstract

The effect of the two inorganic pigments widely used for coating of high-end ink-jet papers—amorphous silica and precipitated calcium carbonate (PCC)—and poly(vinyl alcohol) binder on ink-jet paper and print quality was studied. Multivariate analysis of results revealed that the type and the proportion of the pigments significantly influences several paper and print characteristics as determined by wicking, mottling, striking through, ink absorption and electrical surface resistance. Water absorption characteristics of paper are not related to ink-jet print quality but rather to the hydrophobicity/hydrophilicity of base paper sheet. The effect of the coat weight on the printed paper performance is considerable only in cases where 100% silica or silica–PCC combinations were applied. In coatings with 100% PCC, this effect is much smaller in comparison to that of the pigment itself.

Keywords: Ink-jet paper; Print quality; Coating pigments; Silica; Precipitated calcium carbonate; Multivariate analysis

1. Introduction

Ink-jet (in the following text: IJ) papers that are available on the market today are predominantly uncoated, multipurpose papers. They are suitable for most routine applications. However, uncoated, surface sized grades do not allow for high-end print and image appearance. The latter is achieved by applying special coating formulations onto the paper surface. In this study two coating pigments—silica and precipitated calcium carbonate (PCC)—together with different amounts of a binder—poly(vinyl alcohol) (PVOH)—were investigated in order to evaluate influence of coated paper parameters on the IJ paper and on the resultant print quality. The results were interpreted using multivariate methods, principal components analysis (PCA) and cluster analysis.

1.1. Pigments for ink-jet paper

Demands for high-end IJ papers are manifold. They must provide good fixation of the ink to the paper surface, quick ink solvent absorption and minimize ink bleeding and wicking while at the same time retaining favourable gloss, ink optical density and colour fidelity [1]. Image print-through to the back side of the paper should be kept as low as possible. The image should also resist smearing when wetted. Coating formulations fulfilling such diverse tasks and providing high print quality

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usually consist of silica and/or PCC as pigments and PVOH as a binder.

Amorphous silicas (precipitated and fumed) exhibit high porosity, hydrophilicity and surface area [2]. Due to these properties, fast absorption of the aqueous ink vehicle is achieved, therefore speeding up the ink drying time and increasing the edge sharpness. Potential drawbacks to the use of synthetic silica are its high production costs and the less favourable rheology that it generates in formulation. Also, porous formulations containing silica are inherently weak. Thus, a high-strength binder such as PVOH is needed. PVOH is also valued for its hydrophilicity, which promotes absorption of the aqueous ink vehicle.

Recently, another specialty pigment for IJ papers has been offered—precipitated calcium carbonate (PCC). Due to its controlled manufacturing parameters PCC can be effectively used as an alternative to silica-based pigments. Concerning the fixation of IJ inks onto the coated paper surface, it has been proposed [3] that unlike silica coatings, which hold the fluid phase including the dye of IJ ink, specialty PCC holds only the dye and allows the fluid phase to pass through.

1.2. Principal components analysis

Principal components analysis (PCA) is a mathematical method that transforms complex multivariate data set into a new perspective in which the most important information is made more obvious. It enables identification of natural patterns or structures in the data by visualizing the relationships among the samples as well as among the variables studied.

PCA is conceptually similar to some other multivariate methods, such as correspondence analysis, singular value decomposition, eigenvector analysis and factor analysis [4]. It is based on a construction (extraction) of a new set of variables called principal components (PCs) that are completely uncorrelated—orthogonal—to each other.

A score s_{ip} is a projection of sample i along a principal component PCp and is, mathematically speaking, a linear combination of the original variables [5]:

$$s_{ip} = \sum_j v_{jp} \cdot x_{ij} \tag{1}$$

Here v_{jp} is the *loading* of variable j on PCp and x_{ij} is the value of the ith object for original variable j. In matrix notation one can write:

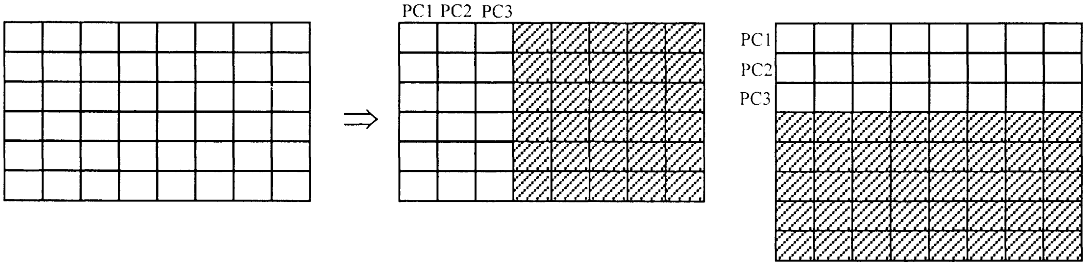
$$\mathbf{S} = \mathbf{X} \cdot \mathbf{V} \tag{2}$$

Here **S**, **X** and **V** are the matrices of scores, the original variables and the loadings, respectively. The equation can be rearranged into:

$$\mathbf{X} = \mathbf{S} \cdot \mathbf{V}^{\mathrm{T}} \tag{3}$$

In practice, this means that the data matrix **X** can be decomposed into a product of two matrices, one about the samples (**S**) and the other containing information about the variables (**V**). $\mathbf{V}^{\mathrm{T}}$ denotes the transposition of matrix **V**, obtained from **V** by switching its rows and columns. Calculation of these new matrices, that is, extraction of PCs proceeds successively so that each of the PCs captures as much as possible of the variation that has not been explained by the former PC: PC1 maximizes the covariance in the original data set and the following PCs maximize the covariance in the residual matrices left after extracting the former PCs. The decomposition is graphically displayed in Fig. 1. The **S** matrix contains the scores of m samples on n principal components: rows represent individual samples and columns denote principal components. The square $\mathbf{V}^{\mathrm{T}}$ matrix consists of the loadings (=columns) of the n original variables on the n latent variables (=rows). By retaining only the first few significant components, in our case PC1 to PC3, one eliminates irrelevant information since higher components contain predominantly data noise (grey parts of matrices).

The way in which PCA is used most frequently is by graphically displaying the calculated scores and loadings in the coordinate system of a first few PCs. Such interpretation enables visualization of patterns in the data and reveals similarities and dissimilarities between individual samples as well as relationships between the original variables.



$$\underset{m \times n}{\mathbf{X}} = \underset{m \times n}{\mathbf{S}} \cdot \underset{n \times n}{\mathbf{V}^{T}}$$

Fig. 1. Decomposition of matrix X into matrices S and V^T.

Principal components can be regarded as "composite" variables constructed from original ones as their linear combination. Sometimes it is possible to assign a physical meaning to the first few principal components.

1.3. Cluster analysis

Cluster analysis is a data analysis technique that allows one to organize a set of observations (objects, samples) described by variables, into groups. It encompasses a number of different classification algorithms, such as tree clustering, two-way joining or K-means clustering [6]. In the tree clustering algorithm objects are joined together into successively larger clusters according to a certain measure of similarity or distance. Ward's method [7], as applied in this study, uses an analysis of variance (ANOVA) approach to evaluate the distances between clusters. A typical result of tree clustering is a dendrogram or hierarchical tree (Fig. 2). Here the horizontal axis denotes the linkage distance. In the beginning, each object (i.e. sample or case) represents a class by itself (left part of the plot). By linking together more and more objects and aggregating larger and larger clusters of increasingly dissimilar elements we finally come to a point where all objects are linked together (right part of the dendrogram). The more similar two objects or groups of objects are, the closer to the left of the dendrogram they are linked. As the result of a successful tree clustering analysis, one can detect and interpret individual clusters or branches.

2. Experimental

In the study two fundamentally different wood-free base paper types were examined: an unsized paper (samples designated as V) and a rosin sized (samples S) paper. These samples were coated, using a benchtop drawdown rod coater, with coating formulations consisting of one or two pigments—amorphous silica and/or PCC—and a PVOH binder (Table 1). Rather than making optimized formulations, only simple pigment–binder blends were set up to illustrate differences in pigments' behaviour. Also, the amount of PVOH—30–50 parts per hundred parts of pigment—was higher than that used in real high-end IJ coatings, especially for the coating colours with PCC. All of the formulations were prepared at 21% solids. The coat weights ranged from 3.4 to 6 g/m^2.

In order to evaluate the IJ print quality, a test form was printed onto the paper sheets with an EPSON Stylus Color 900 printer. Printing parameters were kept at their default values with the resolution set to 720 dpi.

Table 1
Coating formulations

Ingredients (parts)	Formulation		
	F	G	H
Silica A	80	–	50
Silica B	20	–	–
Precipitated calcium carbonate (PCC)	–	100	50
Poly(vinyl alcohol) (PVOH)	30	50	50

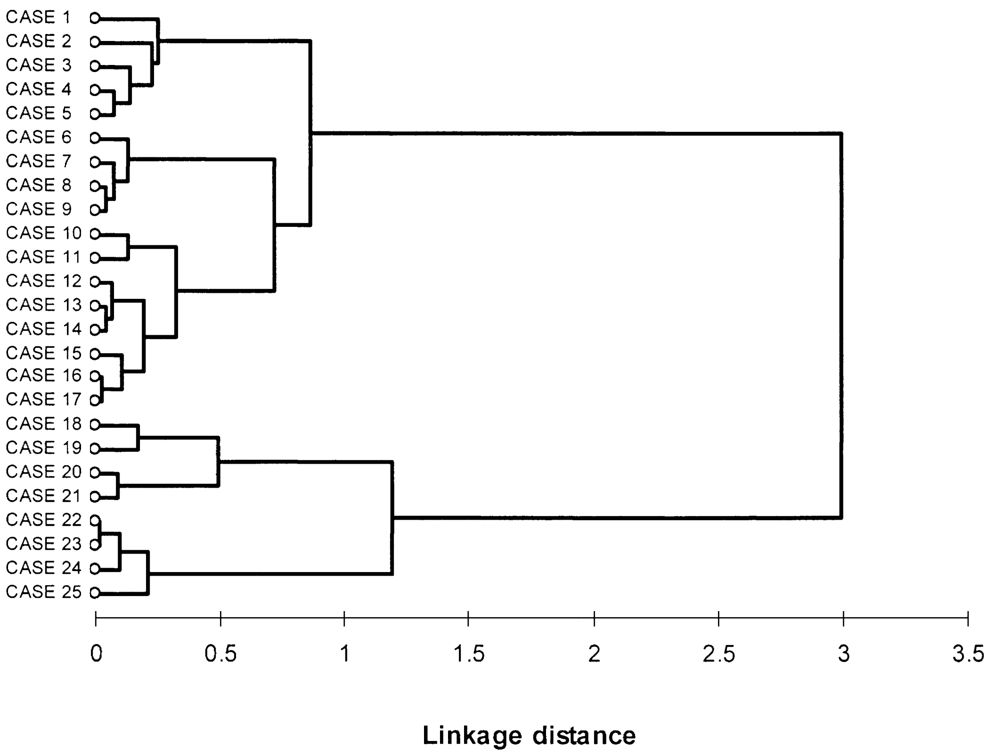


Fig. 2. Tree clustering of samples.

Altogether 11 parameters that described paper samples, before as well as after IJ printing process, were measured (Table 2). The characteristics of non-printed specimen were determined through evaluation of porosity (POROS), electrical surface resistance (RESIST_NP), Cobb value (COBB) and PDA value (PDA). The latter was obtained from the shape of ultrasound intensity vs. time curve using a Penetration Dynamics Analyser and is an indication of water penetration rate into the paper sheet structure. IJ print quality was assessed by performing the classical offset K&N ink absorption

Table 2
Measured parameters of coated and printed papers

	Variable		Range
Non-printed paper samples	Porosity (Gurley); s	POROS	56–300
	Electrical resistance; Ohm	RESIST_NP	1.0–7.2
	Water absorption (Cobb), g/m^2	COBB	16–100
	Water penetration rate;	PDA	67–5315
Printed paper samples	K&N ink absorption;%	K&N	24.9–54.3
	Striking through;	STRIKE	0–2
	Electrical resistance; Ohm	RESIST_P	0.6–2.1
	Wicking;	WICK	5.0–35.0
	Bleeding;	BLEED	11.8–35.3
	Mottling;	MOTTL	33–43
Coating	Coat weight; g/m^2	COATW	3.4–6.0

test (KN), a visual evaluation of ink striking through (STRIKE), electrical surface resistance (RESIST_P) measurements and using image analysis techniques for determination of wicking (WICK), bleeding (BLEED) and mottling (MOTTL). Since we also wanted to examine effect of coat weight (COATW) on IJ paper performance, this variable was also monitored.

3. Results

The correlation coefficients table, showing linear relationships within each pair of the 11 variables examined (Table 3), reveals several strong interactions. From the corresponding values one can, for example, see that an increase in wicking is accompanied by a substantial reduction in K&N ink absorption ($r = -0.93$) and an about equally strong increase in coated paper porosity ($r = 0.93$). To explore such dependencies in more depth, PCA was run on a data matrix consisting of 12 cases—paper samples differing in base paper sizing degree (V or S), coating pigment type (F, G and H) and coat weight (from 3.5 to 6.0 g/m^2)—and 11 variables—paper structural, sorptive and printing properties.

Results of the analysis indicate (Fig. 3) that the first four "composite" variables—PC1, PC2, PC3 and PC4—together account for nearly 94% of total variability in original data. The remaining seven higher principal components—PC5–PC11—

Table 3
Linear correlations among variables

	POROS	RES_NP	COBB	PDA	K&N	STRIKE	RESIST_P	WICK	BLEED	MOTTL	COATW
POROS	1.00										
RESIST_NP	0.74	1.00									
COBB	−0.02	0.24	1.00								
PDA	0.01	0.27	1.00	1.00							
K&N	−0.91	−0.76	−0.11	−0.13	1.00						
STRIKE	0.78	0.64	0.42	0.44	−0.85	1.00					
RESIST_P	0.95	0.79	0.04	0.08	−0.86	0.79	1.00				
WICK	0.93	0.75	0.00	0.04	−0.93	0.79	0.93	1.00			
BLEED	0.53	0.37	0.20	0.16	−0.46	0.35	0.39	0.35	1.00		
MOTTL	0.84	0.65	0.24	0.26	−0.84	0.76	0.77	0.83	0.57	1.00	
COATW	−0.10	−0.47	0.09	0.09	0.34	−0.13	−0.11	−0.22	0.06	−0.02	1.00

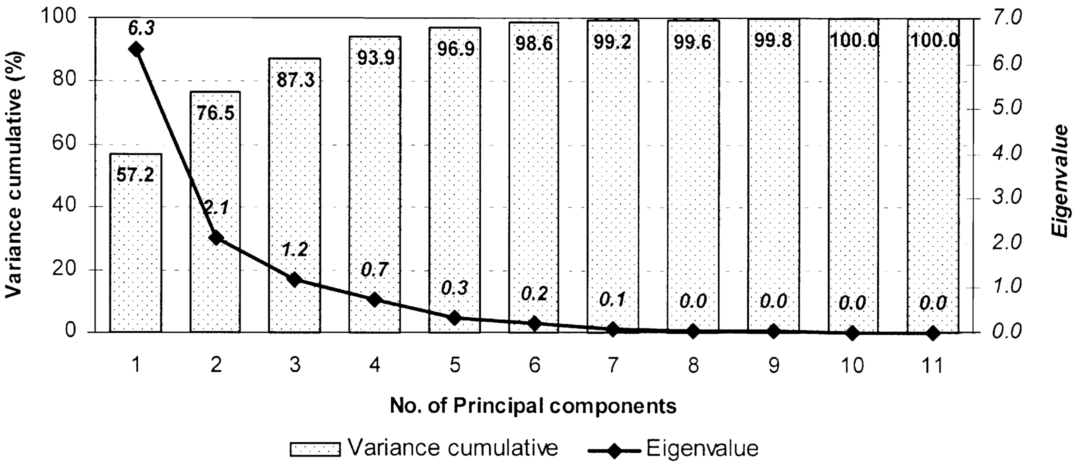


Fig. 3. Plot of cumulative variance and eigenvalues for individual PCs.

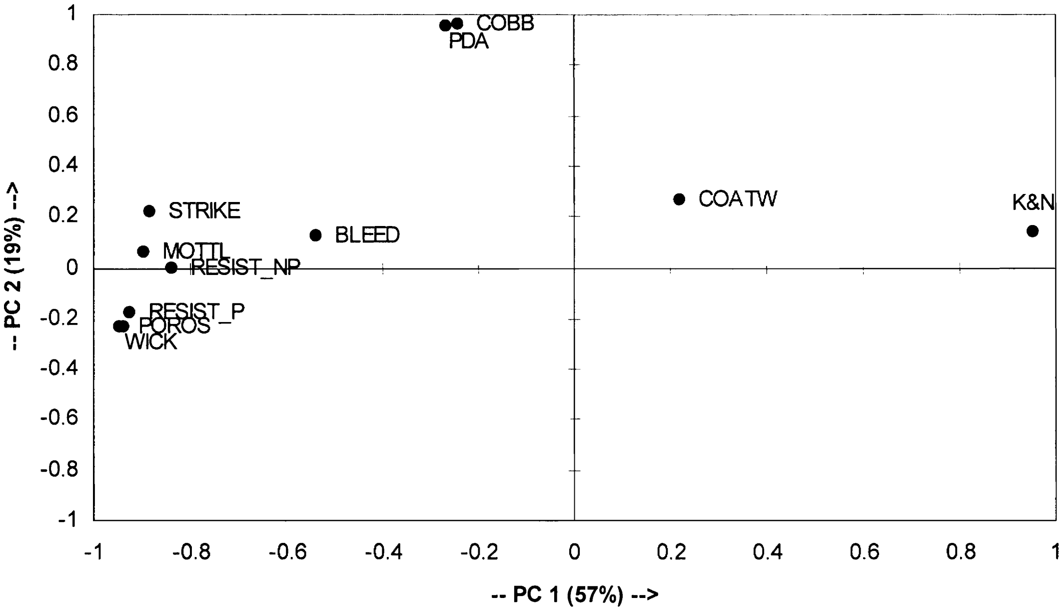


Fig. 4. Variables in PC1–PC2 plane.

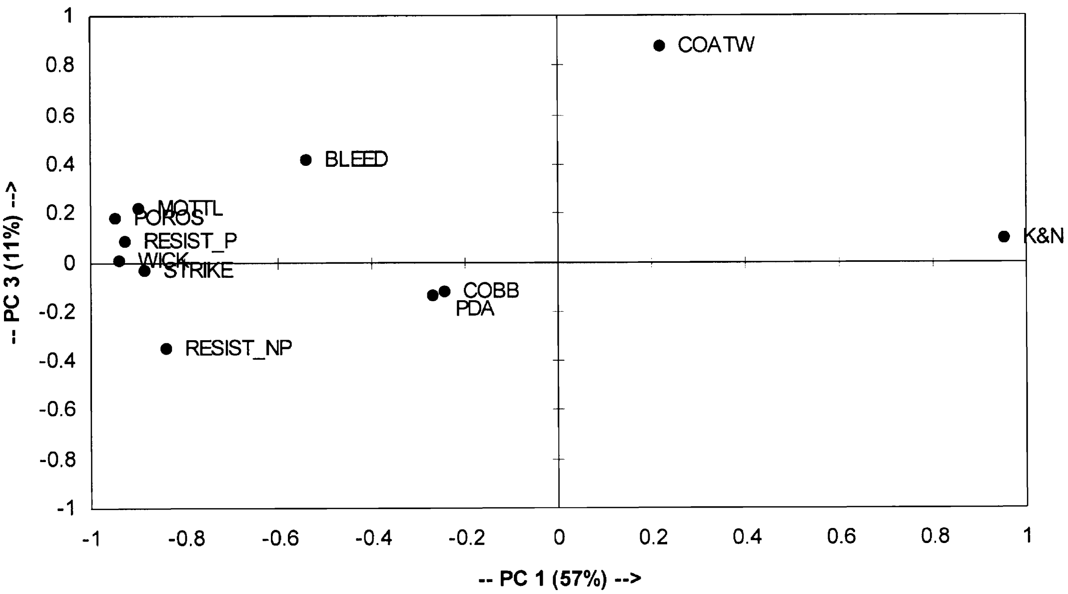


Fig. 5. Variables in PC1–PC3 plane.

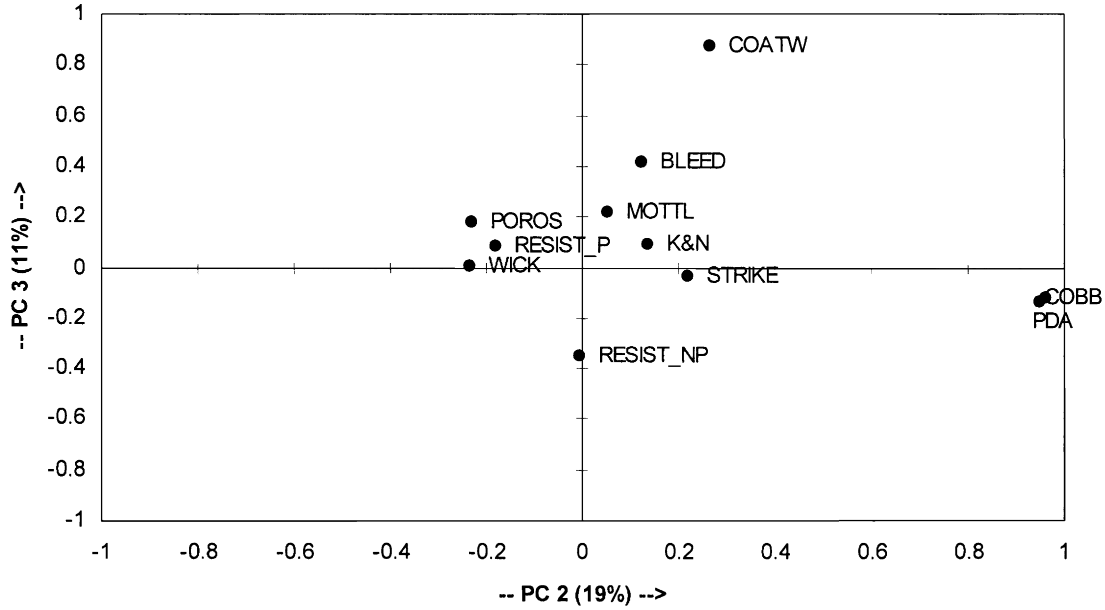


Fig. 6. Variables in PC2–PC3 plane.

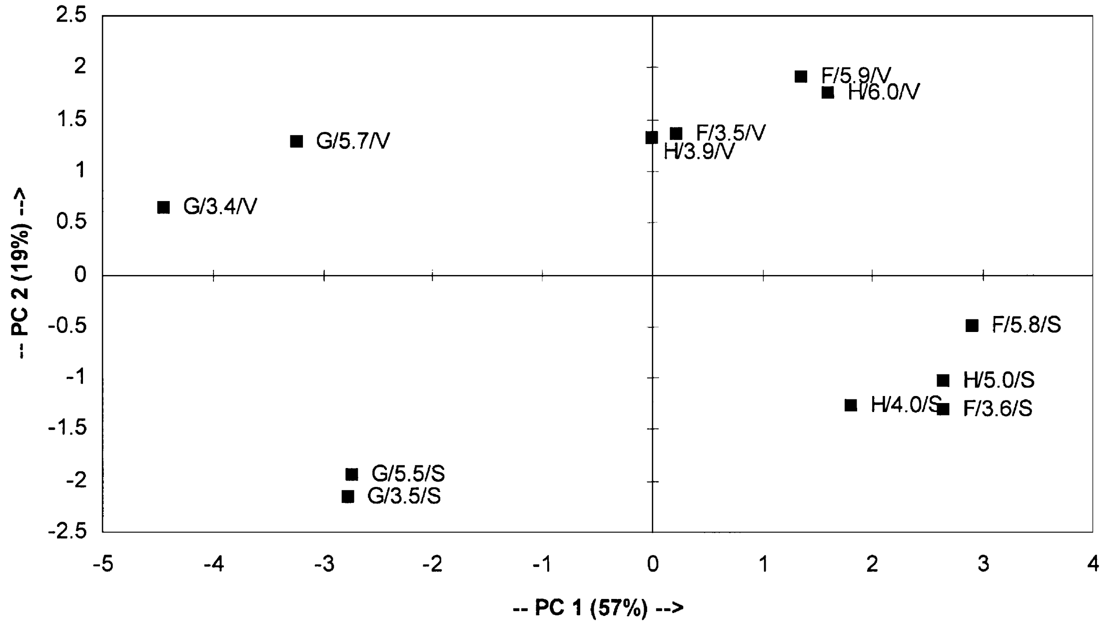


Fig. 7. Samples in PC1–PC2 plane.

explain only a very small portion of information and since their *eigenvalues* are below 1.0, they can be neglected. In fact, most of the relevant information (87%) can be represented by the first three principal components. Diagrams showing correlations between initial variables and the first three principal components—*loading* plots—as well as diagrams representing relationships within samples—*score* plots—are displayed in Figs. 4–9.

From the calculated squared *loadings* values, another interesting diagram can be constructed (Fig. 10) that displays contributions (in %) of individual original variables to the principal components. Another useful plot from which similarities as well as differences among samples can be interpreted is a dendrogram (Fig. 11) produced as a result of cluster analysis. Both diagrams will be discussed in detail in the following section.

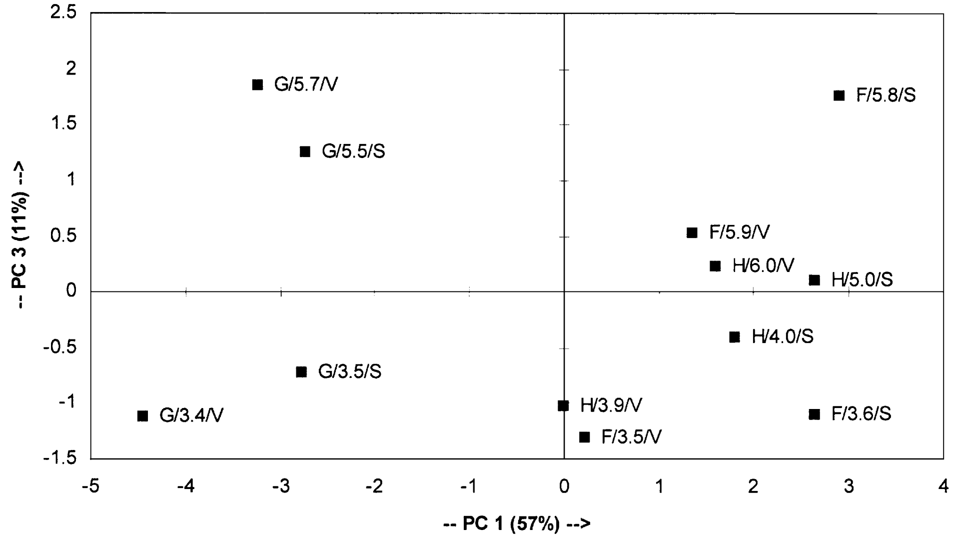


Fig. 8. Samples in PC1–PC3 plane.

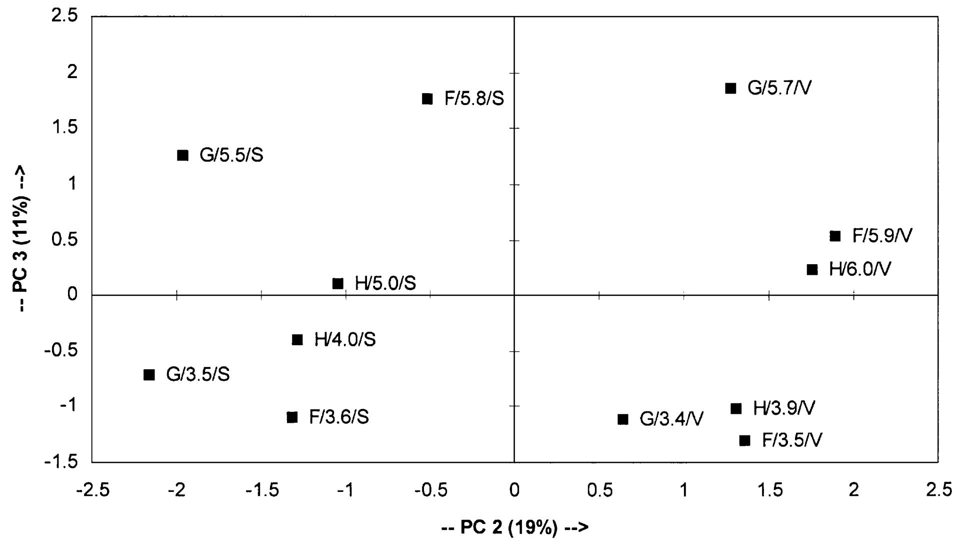


Fig. 9. Samples in PC2–PC3 plane.

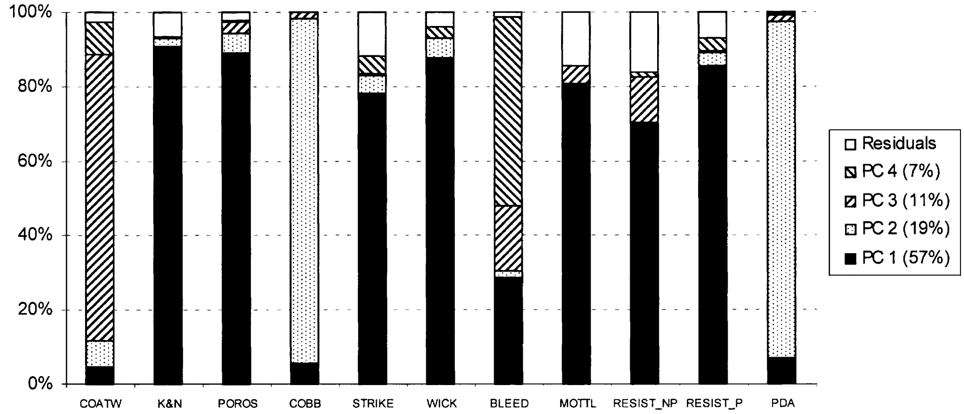


Fig. 10. Contribution of individual variables to principal components.

Constellation of individual variables in PC1–PC2 plane (Fig. 4) shows some distinctive patterns. PC1 is the horizontal axis and PC2 is the vertical axis. First of all, there is an evident grouping of points on the left side of the diagram—STRIKE, MOTTL, RESIST_NP, RESIST_P, POROS and WICK—indicating strong linear correlations among these variables: papers with high porosity (POROS) exhibit increased electrical surface resistance both on non-printed samples (RESIST_NP) as well as on printed samples (RESIST_P) and are characterized by excessive wicking (WICK), bleeding (BLEED) and striking through (STRIKE). These variables all tend to have high negative loadings on PC1 and very small contribution (i.e. orthogonal projection) to PC2 and therefore represent PC1 to a large degree. The variable on the opposite side of the diagram—the K&N ink absorption value—also strongly determines PC1 but is negatively related to the above mentioned variables: its increase is accompanied by a decrease in STRIKE, MOTTL, RESIST_NP, RESIST_P, POROS and WICK values.

From the position and proximity of points COBB and PDA it is clear that these two variables are very closely related to each other (see Table 3: $r = 0.996$) but not to any other variable. The physical meaning of PC2 has obviously much to do with these two parameters, since they are the only ones that have high contribution to this axis.

The coat weight (COATW) parameter is located relatively close to PC1–PC2 origin meaning that it can be related neither to PC1 nor to PC2. If the PC1–PC3 loading diagram (Fig. 5) is examined, however, it is apparent that this variable determines significantly the third principal component, PC3, since the contribution to this principal component is considerable.

Similar conclusions can be drawn when observing Fig. 10, which graphically shows breakdown of original variables by the first four principal components. With the exception of bleeding, whose contribution is divided between PC1, PC3 and PC4, all other variables seem to grasp the essence of more or less a single principle component: variables KN, POROS, STRIKE, WICK, MOTTL, RESIST_NP and RESIST_P of PC1, COBB and PDA represent PC2 and COATW represent PC3. Contribution of variables to higher axes (PC5–PC11), designated as *Residuals*, is negligible.

Score diagrams give us indication of similarities/dissimilarities and patterns among samples. PC1 in the PC1–PC2 score plot (Fig. 7) separates points into two groups: samples on the left part of the diagram designated as G/5.7/V, G/3.4/V, G/5.5/S and G/3.5/S form one cluster and F and H samples on the right belong to the other one. From what has been previously said about the variables having high—positive or negative—contributions to PC1 and bearing in mind the fact that G samples were coated with PCC, it is possible to conclude that physical meaning of the first principal component is related to coated paper surface characteristics and, consequently, to ink behaviour. These phenomena are decisively influenced by the coating pigment type. Wherever paper was coated with PCC only, samples are marked by high porosity, ink-jet ink striking through, mottling and wicking are pronounced, penetration rate of K&N offset ink, on the other hand, is low. Non-printed samples as well as ink-jet printed samples show high electrical resistance.

Similarly, PC2 splits samples into an "upper" and a "lower" group. The former consists entirely of non-sized samples (V), the latter consists of sized (S) samples only. The second principal component is apparently related to hydrophilicity/hydrophobicity of the base paper since the Cobb value and the PDA integral are both an indication of water penetration rate into the paper sheet. Note that the principal components are, by definition, orthogonal, i.e. uncorrelated to one another, meaning that factors influencing PC1 are different from those representing PC2.

Eleven per cent of the total data variability can be explained by PC3. Since the coat weight (COATW) is the key parameter through which this principal component can be interpreted, it is natural that, in the PC1–PC3 *score* plot (Fig. 8), it separates samples according to their coat weight: from 5.7 g/m^2 in G/5.7/V (highest positive score) to 3.5 g/m^2 in F/3.5/V (highest negative score).

In order to study how individual samples are similar to each other or to what extent (and why) they differ, it is—apart from looking at PCA score plots—instructive to observe dendrogram produced by cluster analysis (Fig. 11). Samples having the shortest linkage distance are the most similar to each other: G/5.5/S and G/3.5/S; F/3.6/S, H/4.0/S and H/5.0/S; H/6.0/V and F/5.9/V; H/3.9/V and F/3.5/V—see also PC1–PC2 score plot (Fig. 7). The bigger the linkage distance, that is, the further to the right, the less similar (groups of) samples are being liked to one another. In the end, even the two most distant clusters are linked.

A closer inspection of samples' agglomeration reveals some more interesting points. This is seen in a study of gradual grouping of the last four samples: H/6.0/V, F/5.9/V, H/3.9/V and F/3.5/V.

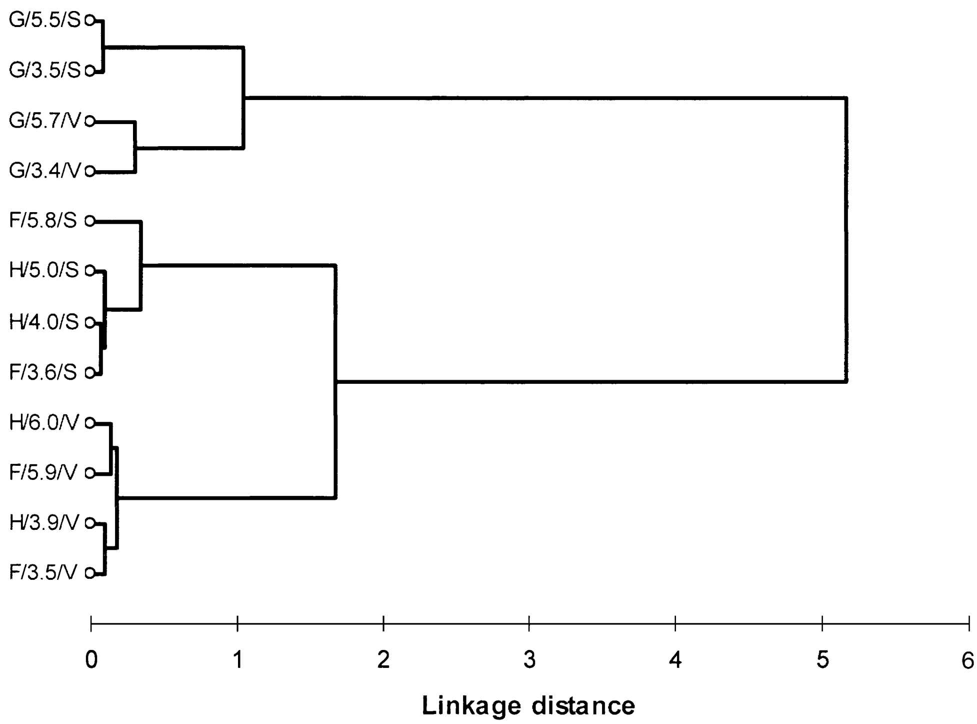


Fig. 11. Dendrogram—similarities among samples.

Earliest linkages—H/6.0/V and F/5.9/V; H/3.9/V and F/3.5/V—are obviously due to the similarities in coat weights. Although not being coated with the same coating pigment, samples H/6.0/V and F/5.9/V have more in common to each other than with the other "partner" of the same pigment type but considerably lower coat weight. Note that all four papers are unsized. Similar considerations can also be applied to the middle four sized samples—F/5.8/S, H/5.0/S, H/4.0/S and F/3.6/S—although the picture here is less clear. Linkage at a "distance" of 1.7 indicates that there is a distinctive separation of both groups with respect to the papers' hydrophilic/hydrophobic character.

While for the paper samples coated with PCC—G/5.5/S, G/3.5/S, G/5.7/V and G/3.4/V—the linkage at a distance of 1.0 also connects the two sized samples with the two unsized ones, the left-most, earliest linkage of G samples shows an important difference when compared to F and H papers. A decisive similarity criterion is the type of pigment used in coating rather than the coat weight: G/3.5/S is more similar to G/5.5/S than would be, for instance, to F/3.6/S. The right-most linkage at 5.2 shows that the four samples coated with PCC form one distinctive group compared to silica- and PCC–silica-coated papers, in which the type of pigment does not determine their characteristics in such a pronounced way.

The results of this study confirm that the correct pigment selection and pigment:binder ratio are of vital importance for the IJ print quality. Printed paper parameters such as wicking, mottling, striking through, K&N absorption and electrical surface resistance are decisively determined by the type and proportion of pigments in a coating formulation. It has been demonstrated that high paper porosity and electrical resistance are accompanied by pronounced mottling, wicking and ink strike through. Markedly poorer performance of precipitated calcium carbonate with respect to two silica pigments is due to lower PCC quality and lower surface area compared to silicas. The recommended amount of binder lies for PCC between 7 and 15 parts per hundred parts of pigment, while for silica these numbers are much higher—between 30 and 40 parts. As the PCA reveals, water absorption characteristics of paper expressed through Cobb and through PDA values are not related to IJ print quality but rather to the hydrophobicity/hydrophilicity of the base paper sheet, i.e. its degree of sizing. The coat weight affects the printed paper performance only to some extent. Only in the case of papers that had been coated with 100% PCC, is the influence of coating pigment much more important than that of coat weight.

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