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PHYSICO-CHEMICAL CHARACTERIZATION OF DETRIMENTAL PAPER MACHINE DEPOSITS

FIZIKALNO-KEMIJSKA KARAKTERIZACIJA MOTEČIH OBLOG NA PAPIRNIH STROJIH

Janja Zule, Jožica Dolenc

Pulp and Paper Institute, Bogišičeva 8, 1000 Ljubljana, Slovenia
janja.zule@icp-lj.si; jozica.dolenc@icp-lj.si

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In order to find effective solutions to the problems of depositing materials on papermaking equipment, qualitative and quantitative analysis of deposits has to be performed. Thus, the sources of contaminants, as well as the causes of their agglomeration can be established in connection with applied technological parameters.

Due to the importance of these problems, an analytical procedure for identification and quantitative evaluation of detrimental materials has been introduced at the Pulp and Paper Institute in Ljubljana. According to the scheme, the contents of ash and THF extract are analysed in deposit samples, and afterwards the IR spectra of both are recorded. In addition, THF extract is analysed by GC an GPC. The exact chemical composition of samples is possible to determine only by combining the results of different methods and by comparing them with chromatographic and spectroscopic data for applied chemical additives. Numerous analyses have proved that most detrimental and deposit-causing materials are wood lipids, synthetic polymers and different ingredients of the papermaking additives.

Some typical cases of efficient chemical analysis of detrimental deposits from different papermaking systems are presented in this work.

Key words: paper machine, deposits, wood lipids, synthetic polymers, inorganic pigments, analytical methods

Učinkovito reševanje problematike nastajanja motečih oblog na papirniški strojni opremi zahteva temeljito analizo njihove kvalitativne in kvantitativne sestave. S tem je možno ugotoviti izvor motečih snovi, ob hkratnem upoštevanju tehnoloških parametrov pa tudi vzroke njihovega kopičenja.

Zaradi aktualnosti problematike v papirnicah smo na Inštitutu za celulozo in papir v Ljubljani izdelali analizni postopek za identifikacijo in kvantitativno vrednotenje komponent, ki sestavljajo obloge. Tako v vzorcih najprej določimo vsebnost pepela in tetrahidrofuranskega (THF) ekstrakta ter posnamemo IR-spektre. THF-ekstrakt analiziramo tudi s plinsko in gelsko kromatografijo. Na osnovi kombinacije rezultatov različnih metod in primerjave z zbranimi podatki o uporabljenih papirniških sredstvih lahko ugotovimo natančno kemijsko sestavo vzorcev. Analize so pokazale, da so najpomembnejši povzročitelji oblaganja lesni lipidi, sintetični polimeri in posamezne komponente pomožnih sredstev.

Predstavljamo nekaj tipičnih primerov uspešnega reševanja problematike nastajanja oblog v različnih tehnoloških sistemih.

Ključne besede: papirni stroj, obloge, lesni lipidi, sintetični polimeri, anorganski pigmenti, analizne metode

1 INTRODUCTION

The main raw materials in paper industry are primary fibers (wood fibers, cellulose), recycled fibers (waste paper) and different inorganic and organic chemical additives which help improve paper properties so that the product may be applied in any chosen way. All the incoming materials may contain organic impurities, whereas some are actually composed of constituents which may become detrimental under certain technological conditions. Hydrophobic particles which cause a build-up of sticky deposits on different parts of paper machine equipment are the most problematic. During the drying process, deposits most often agglomerate on sieves and felts which serve as a support for a newly formed paper web. In worst cases, they cause the web to break and production needs to be stopped for cleaning, which reduces process efficiency and increases the costs. Paper quality may sometimes be very poor due to the appearance of dark spots on the surface which indicate the paper's unsuitability for high quality printing purposes [1,2].

The most commonly encountered sticky impurities or "stickies" are resin from fresh wood fibers, as well as the remains of printing inks, binding agents, coatings, adhesives and foils originating from waste paper. Some chemical additives, such as fillers, sizing agents, surfactants, wet strength resins, waxes and the like may also contribute to the system pollution if they are not effective enough or fully bound in paper structure. All these compounds either travel through the papermaking system tied to fibers, or else they may be dispersed or dissolved in process water. At sudden changes of technological parameters such as pH, temperature, turbulence, etc., the physico-chemical equilibrium is destroyed, enabling precipitation of stickies and other present materials on different parts of paper machines.

Chemical composition of typical deposits is usually very heterogenous as they can consist of inorganic and

organic particles, natural and synthetic components, low molecular weight compounds and polymers [3].

Some potentially detrimental substances originating from the most important papermaking raw materials are listed in **Table 1**.

Table 1: Chemical composition of impurities
Tabela 1: Kemijska sestava nečistoč

Fresh fibers	Recycled fibers	Additives
triglycerides	polyethylenes	resin acids and derivatives
waxes	polystyrenes	fatty acids and derivatives
steryl esters	styrene-butadiene copolymers	hydrocarbons
sterols	styrene copolymers	alkyl ketene dimers
fatty alcohols	polyamides	epichlorohydrin
resin acids	polyacrylates	starch
fatty acids	polypropylenes	silicones

Beside stickies, the most characteristic and often predominant constituents of paper machine deposits are also fiber fragments and inorganic fillers such as calcium carbonate, kaolin and talc which are extensively used in paper industry.

A proper and simultaneous chemical analysis of deposits and raw materials is of a great importance for establishing the origin of detrimental compounds and suitability of individual materials for the production of specific paper grades.

A detailed characterization of deposits may be very difficult due to the complexity of their chemical structure. Various separation schemes and analytical techniques, such as chromatographic GC, GC/MS, Py-GC/MS and GPC and spectroscopic UV/VIS, IR and NMR should be used. Only by combining the results of different methods, a thorough insight into the structure of such samples can be obtained [4].

The purpose of our systematic research was to develop a simple and quick analytical procedure for separation and identification of detrimental substances that constitute paper machine deposits in order to find the causes for their formation in specific technological environments.

The analytical scheme and some typical examples of solving the problems of deposit formation in different papermaking systems are presented in this paper.

2 EXPERIMENTAL

2.1 Samples

The following typical deposit samples from four different production processes were analysed:

– deposit from printing paper production where fresh softwood fibers were used (3.1)
– deposit from board production where 100 % recycled fibers were used (3.2)

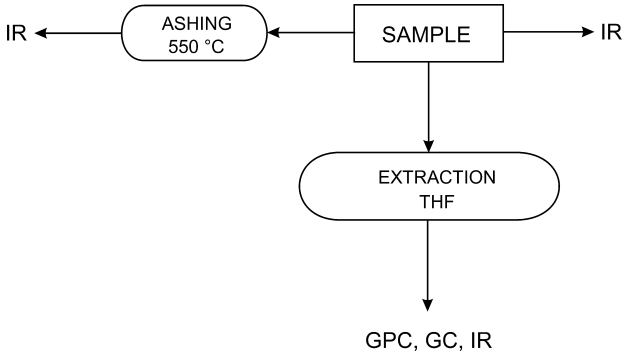

Figure 1: Analytical scheme
Slika 1: Shema analiznega postopka

– two deposits from specialty paper production where fresh softwood and hardwood fibers were used (3.3 and 3.4)

2.2 Analytical procedure

Each sample was air-dried and homogenized. Inorganic and organic portions were determined by ashing the sample at 550 °C. IR spectra of the original and ashed samples were subsequently recorded. All deposit samples were also extracted by organic solvent tetrahydrofuran (THF), after which the extract content was determined. IR spectra, GC and GPC chromatograms of the extracts were recorded and evaluated as well (**Figure 1**).

2.2.1 Preparation of THF extract

A suitable quantity of air-dried sample was Soxhlet extracted for 8 h, or at least as long as the extract became colourless, upon which it was evaporated, vacuum dried and quantitatively evaluated.

2.2.2 IR spectroscopy

The spectra of THF extracts were recorded as films on NaCl plate, while the spectra of solid deposits and ashes were recorded from KBr pellets. The scanning range was between 4000 cm^{-1} and 400 cm^{-1}. Perkin Elmer 783 IR spectrometer was used for all recordings.

2.2.3 Gas chromatography (GC)

THF extracts were redissolved and methylated by gaseous diazomethane to convert free organic acids into the corresponding methyl esters. GC chromatograms were recorded under the following experimental conditions: injector split/splitless 250 °C; capillary column SPB-1 (15 m or 25 m × 0,25 mm × 0,25 μm); temperature programme 200 °C (2 min), 3 °C/min, 280 °C (10 min); carrier gas N_2 (1,5 ml/min); flame ionization detector (FID) 300 °C.

Relevant chemical standards were used for identification of individual components. All the GC chromato-

grams were recorded on the Hewlett Packard 5890 instrument.

2.2.4 Gel permeation chromatography (GPC)

GPC chromatograms of THF extracts with approximate concentrations of 10 mg/ml were recorded under the following conditions: flow of THF eluent 0,8 ml/min, volume of injected sample 20 µl, chromatographic columns µ Styragel, having nominal pore sizes of stationary phase particles (100, 50, 10 and 5) nm, detectors UV (254 nm) and differential refractometer (Δ RI). Molecular masses of sample components were calculated from the calibration curve, using polystyrene standards.

The chromatographic system consisted of the pump Milton Roy constaMetric 3000 and the detectors Δ RI Milton Roy refractoMonitor IV and Varian ProStarDiode Array detector.

3 RESULTS AND DISCUSSION

Deposit samples differed in the content of inorganic and organic portions, as well as in their chemical characteristics.

3.1 Deposit 1

Sticky greyish-brown deposit from printing paper production accumulated on the long wire of the paper machine. It contained 15 % of ash and 75 % of THF extract. GC and GPC chromatograms indicated that the latter consisted of unsaturated fatty and resin acids as typical components of spruce wood resin. The ash was mainly calcium carbonate. GC chromatogram of the THF extract is presented in **Figure 2** while the identified components (chromatographic peaks) are listed in **Table 2**.

Table 2: Identified compounds
Tabela 2: Identificirane spojine

Peak designation	Chemical compound
1	Palmitic acid
2	Linoleic acid
3	Linolenic acid
4	Pimaric acid
5	Sandaracopimaric acid
6	Isopimaric acid
7	Dehydroabietic acid
8	Abietic acid

The deposit formation was evidently caused by sticky resin from spruce fibers.

3.2 Deposit 2

Dark brown plastic deposits appeared on guide rolls and felts of the machine producing board from 100 % waste paper. The deposit sample contained 19 % of ash

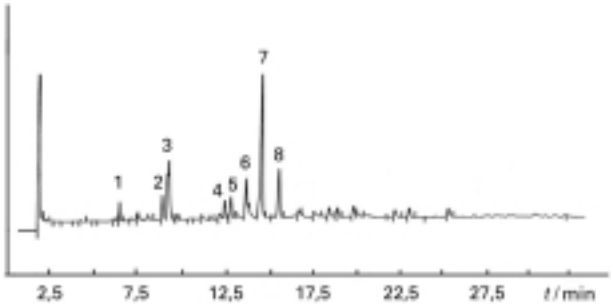

Figure 2: GC chromatogram of the extract of deposit 1
Slika 2: Plinski kromatogram ekstrakta obloge 1

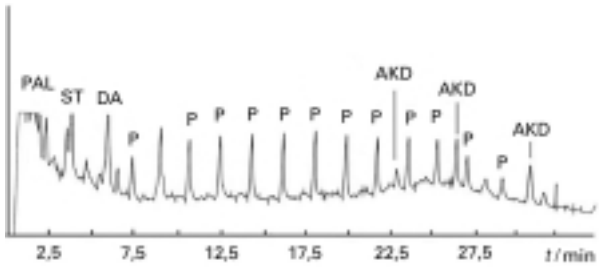

Figure 3: GC chromatogram of the extract of deposit 2 (PAL-palmitic acid, ST-stearic acid, DA-dehidroabietic acid, P-paraffins, AKD-sizing agent)
Slika 3: Plinski kromatogram ekstrakta obloge 2 (PAL-palmitinska kislina, ST-stearinska kislina, DA-dehidroabietinska kislina, P-parafini, AKD-klejivo)

and 23 % of THF extract. GC chromatogram indicated a complex mixture of higher fatty acids (palmitic and stearic), dehydroabietic acid, paraffins and hydrolized components of alkyl ketene dimer (AKD) sizing agent (**Figure 3**), while both polymeric compounds and lower components, having molecular masses 950000, 102000, 48000, 580, 400 and 180, were detected on the GPC chromatogram (**Figure 4**). Polymerics were identified as polyacrylate and polystyrene by the help of the IR spectrum. Inorganic portion was a mixture of carbonates, kaolin and talc.

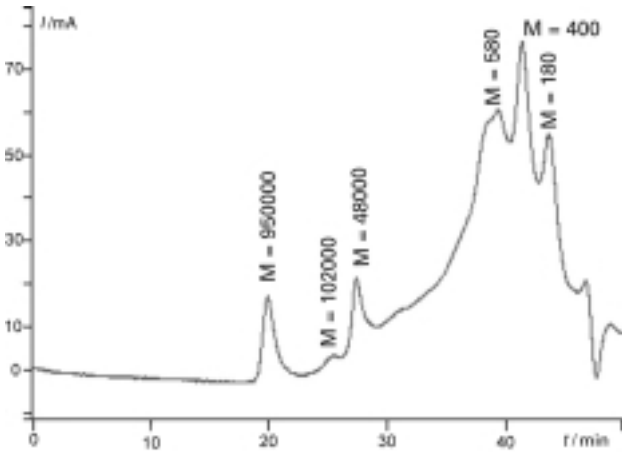

Figure 4: GPC chromatogram of the extract of deposit 2
Slika 4: GPC kromatogram ekstrakta obloge 2

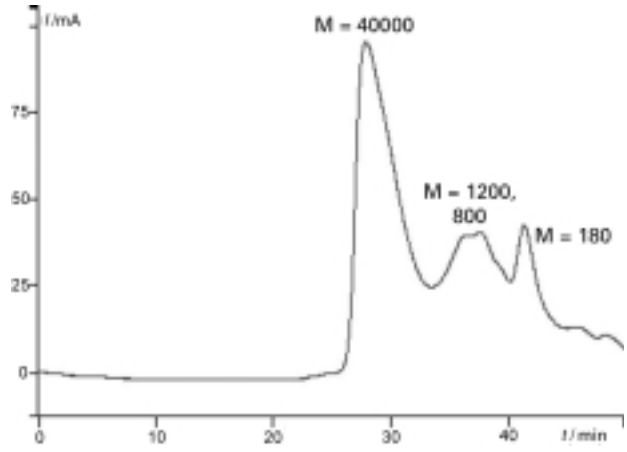

Figure 5: GPC chromatogram of the extract of deposit 3
Slika 5: GPC kromatogram ekstrakta obloge 3

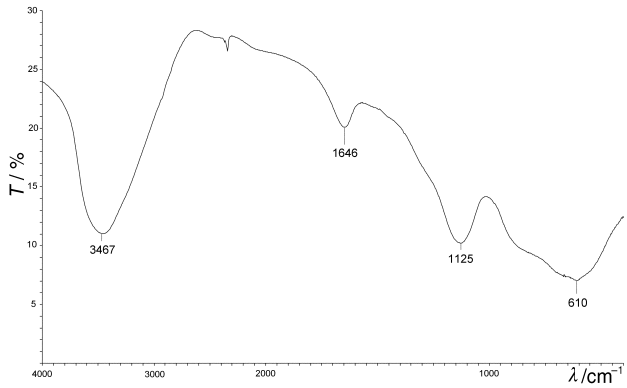

Figure 6: IR spectrum of the ash of deposit 4
Slika 6: IR spekter pepela obloge 4

The results clearly indicate that the most detrimental substances in this case were polymeric residues of acrylate adhesives from waste printed matter. Due to their stickiness and plasticity, they were able to bind other organic and inorganic particles into plastic and very problematic deposits.

3.3 Deposit 3

Grey-blue deposits agglomerated on the blades of the paper machine, producing specialty paper from fresh fibers. Their ash content was 42 % and THF extract amounted to 12 %. GC chromatogram demonstrated the presence of the synthetic AKD sizing agent, while the polymeric material with molecular mass of 40000 was detected by GPC (**Figure 5**).

It was confirmed by the help of UV and IR spectra that the polymeric compound was styrene-butadiene latex which was used as a binding agent in the mixture for surface coating of paper. It entered the system as coated broke which is actually coated paper, recycled immediately after production due to its poor quality or unsuitability for further use. Latex functioned as an adhesive for binding other organic particles and calcium carbonate.

3.4 Deposit 4

Hard and brittle deposits were found on different parts of the paper machine which produced printing paper from fresh cellulose fibers. Their ash content was as high as 49 % while they had only 2 % of THF extract. Typical resin acids could be identified from GC and GPC chromatograms. They were constituents of rosin size which was used for paper sizing. As partial chemical modification of rosin size occurred during the production, which was evident from the corresponding IR spectra of the extract, the sizing agent became more sticky and less soluble in THF. It easily bound kaolin particles which entailed deposit formation. The presence of kaolin was confirmed by the IR spectrum of ash (**Figure 6**).

4 CONCLUSION

The presented analytical procedure enables chemical characterization of numerous inorganic and organic compounds, being the building units of typical paper machine deposits and pollutants of the final product. The results of many analyses of deposit samples from different technological systems clearly indicated that the most detrimental components were hydrophobic particles such as wood lipids, organic polymers, paraffin mixtures and some additives which behaved as binding agents for other present impurities. It was possible to verify the suitability of individual raw materials for the specified paper production by identifying the origin of sticky contaminants.

The fact is that only a profound knowledge of physico-chemical nature and origin of stickies helps find efficient solutions for their elimination from the paper-making systems.

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