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TECHNICAL NOTE

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Enhancement of Ninhydrin- or DFO-Treated Latent Fingerprints on Thermal Paper

ABSTRACT: A new method for enhancement of ninhydrin or 1,8-diazafluoren-9-one (DFO)-treated latent fingerprints on thermal paper will be described. Most thermosensitive surfaces of thermal paper become dark when treated with DFO or ninhydrin petroleum ether (NPB) solution. This effect minimizes contrast between the developed fingerprints and the background. The new method described reduces this dark staining without removing the thermosensitive layer and parts of the developed fingerprints, as occurs with acetone washing. Through the new method, the developed fingerprints appear in sharp lines and high contrast. Extensive tests were performed, leading to an optimized working solution, which charges the paper with a minimum of chemicals, is cheap, and enables a large quantity of papers to be treated in a short time. The working solution contains commercially available, nonvolatile, nitrogenous organic compounds and can be used like the application of NPB solution by dipping.

KEYWORDS: forensic science, fingerprint, detection, thermal paper, ninhydrin, DFO, blackening, whitening

Today, thermal paper is used in cheap printing processes where mobility, fastness, reliability, and low noise are demanded. It especially has an important role in business for bills and receipts in payments.

The intensive use of this material for bills and receipts means that it is becoming more and more important in fingerprint detection. Unfortunately, most thermal paper turns dark on the thermosensitive side when treated with ninhydrin petroleum ether (NPB) or 1,8-diazafluoren-9-one (DFO) solution. This black background staining reduces the contrast to the developed fingerprints, rendering them even useless for fingerprint identification (Fig. 1*c*) (1).

The blackening by ninhydrin solutions is caused by the use of organic polar solvents like ethyl alcohol, acetone, etc. (Fig. 1*a*). With DFO treatment, it is also due to the developing temperature of 80–110°C.

It is well known that blackening of thermal paper caused by NPB treatment can be removed by dipping or washing in acetone. After acetone application, developed latent fingerprints will appear but mostly with a pale and diffuse appearance (Fig. 1*d*).

Our laboratory has been searching for new solutions to this problem for 5 years. During the course of these efforts, we performed experiments with sublimation of ninhydrin in vacuum and introduced the easy-to-use 2-Hydroxy-2-(3,5,5-trimethyl-hexyloxy)-indan-1,3-dione (INON) method from Japan to the German police forces (2,3).

INON is a hemiketal of ninhydrin and isononanol. It is soluble in petroleum ether, even without an additional solubility promoter such as ethyl alcohol. Our examination showed that INON working solutions are much more stable than described in the literature if all work is carried out in aluminum dishes and the solution is stored in aluminum containers. The treatment with INON develops latent fingerprints on both sides of thermal paper without blackening the thermosensitive side (Fig. 1*b*) while conserving the thermal printing without bleeding off the inks of signatures.

In spite of this advantage of INON, we searched for alternatives, in particular, for two reasons:

(A) Thermal paper is not recognized as such and becomes dark due to the inadvertent treatment with the conventional NPB method.
(B) An area of INON-treated paper bears fingerprints and thermal prints, which makes fingerprint identification difficult if the black thermal prints cross and cover the developed fingerprint.

We searched for an easy possibility of permanent decolorization/whitening of these blackened areas without damaging the fingerprints. At the same time, the method must be suitable for large quantities of paper and it must be cheap in application.

For a solution to this problem, we focused on the mechanism of lactone thermal paper. When heated leuco dyes and acid developers react like the indicator phenolphthalein (class of triaryl methane). Leuco dye opens the internal lactone under acid conditions and forms a colored trigonal planar structure. This lactone opening is initiated in thermal paper not only by heat but also by polar organic solvents (4–6).

For these reasons, we focused on basic conditions to reverse the lactone opening and started with basic and proton-accepting compounds from our laboratory like ammonia, diethylamine, trimethylamine, methyl pyrrolidone, and dimethyl sulfoxide, dimethyl formamide. We used them partially in the gas phase, in solution or pure.

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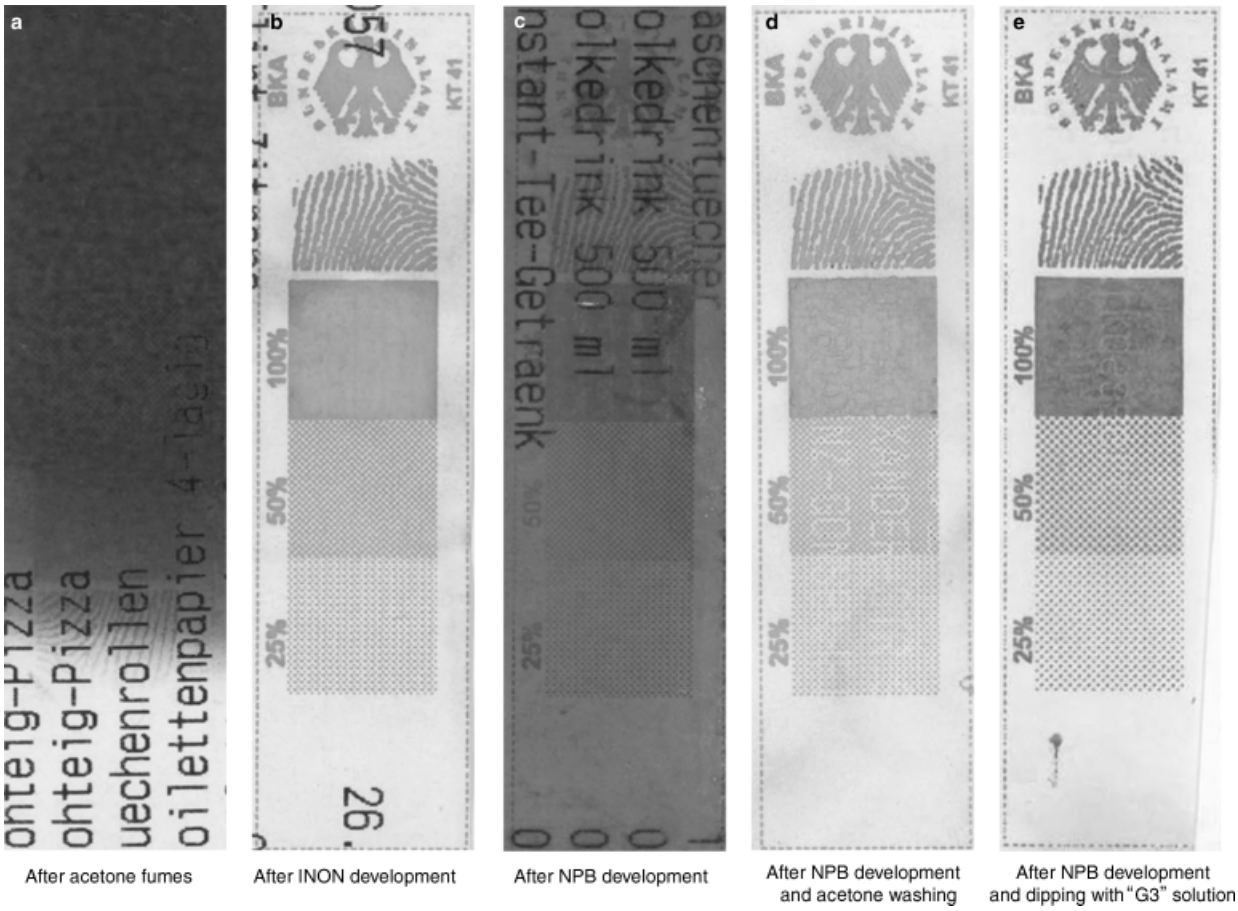


FIG. 1—*(a–e) Test model on thermal paper after different treatments.*

In an atmosphere of diethyl- and trimethylamine, the blackening fades but returns when the thermopaper is taken out of this atmosphere. For the less volatile methyl pyrrolidone, the blackening disappeared for a longer time and ninhydrin-developed fingerprints appear in blue-violet color. This change of color from purple to blue-violet also occurs on normal white paper and changes back through time. Both experimental observations indicate an evaporation of methyl pyrrolidone.

Through these experiments, we learned from colleagues at the Polizeipräsidium Munich and Bavarian Landeskriminalamt of an experiment with a special glue stick, (MGW 57 026, from MGW) on blackened thermal paper. By greasing the black-colored thermosensitive side with this glue stick the blackening fades and the ninhydrin-developed fingerprints appear in a blue-violet color, both stable.

An analysis of the glue stick showed polyvinyl pyrrolidone to be an ingredient. All this information encouraged us to focus our experiments on a whole range of related amides and amines, which led to a new method to increase the contrast of developed fingerprints, which will be presented here.

To speed up the experiments and to reduce the high variance of real fingerprints for better comparison, we used a model of standard test prints. For this, we used an aqueous solution of alanine and printed it using a bubble jet printer in diverse printing forms on porous surfaces, especially diverse papers.

An advantage of printing test prints is the possibility to calculate the printed alanine amount per area. The prints contain several areas (Fig. 2*a–b*):

- area 1 simulates a fingerprint structure;
- area 2 is a full printed field;
- area 3–4 are halftone printed fields; and
- area 5 is an area without printings.

Areas 1, 3, and 4 were used to analyze the precision of details, area 2 for additional densitometric analysis, and area 5 for evaluation of background staining.

As testing material, we used modern bills and receipts from different shops (up to 17 different ones per experiment), fax, filter, white copy, recycled, and brown wrapping paper.

Experimental Setup

Creation of the Model Prints

The model prints were made on thermal paper bills and receipts from several shops as well as filter, white copy, recycled, and brown wrapping paper. On all papers, patterns like Fig. 2 are printed with a solution of alanine using a bubble jet printer (HP DeskJet 550C, HewleH=Packard GmbH, Böblingen, Germany) in 300×300 dpi resolution (7).

For this, the original ink was removed from the HP print cartridge 26, after rinsing several times with distilled water and alanine solution. To clean the printing head, some pages were printed with the filled alanine solution. For the calculation of the average printed amount of alanine per area, a well-defined area was printed and the printed alanine solution was determined by

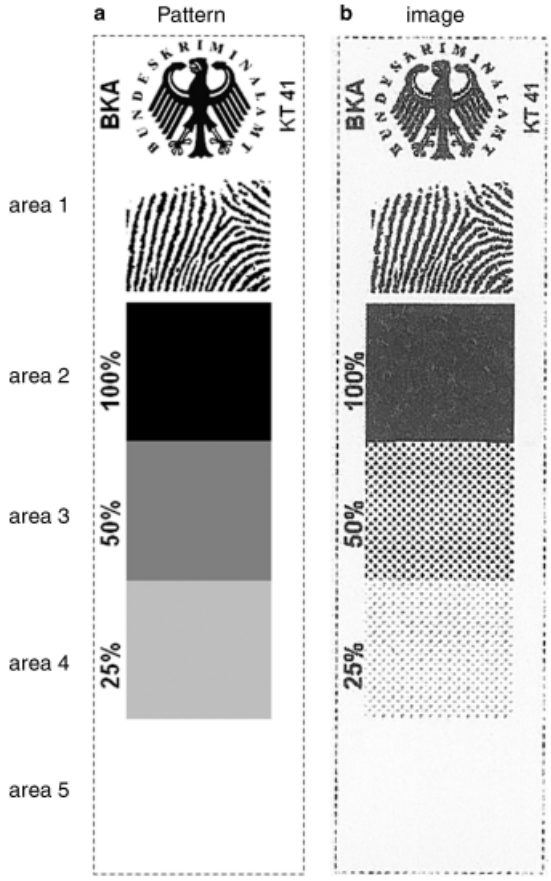


FIG. 2—*(a–b) Finger print model.*

weighting the cartridge before and after printing. For our standard alanine solution with 2.66 g alanine per liter, we calculated 49 ng/mm^2 (0.55 nmol/mm^2) or 49 mg/m^2 (0.55 mmol/m^2). This means 1 g of alanine is sufficient to print an area of 20 m^2. Before using these prints, they were stored for more than 24 h at room temperature.

Processing the Model and Fingerprints by NPB Solution

The testing material was passed slowly through the NPB solution. After drying, the testing material was developed overnight at 60–70% relative humidity and room temperature. The NPB solution (33.7 mM) was prepared by dissolving 15 g (84.2 mmol) ninhydrin in 100 mL ethyl alcohol and filling it up to 2.5 L with petroleum ether.

Processing the Model and Fingerprints by INON Solution

The testing material was passed slowly through the INON solution. After drying, the testing material was developed overnight at 60–70% relative humidity and room temperature. The INON solution was prepared by dissolving 4 g INON (prepared as like described in [3]) in 1000 mL petroleum ether.

Processing the Model and Fingerprints by ThermNin Solution

The testing material was passed slowly through the ThermaNin solution. After drying, the testing material was developed overnight at 60–70% relative humidity and room temperature. The ThermaNin solution was prepared by dissolving 4 g ThermaNin (BVDA International b.v., Haarlem, the Netherlands) in 1000 mL petroleum ether.

Processing the Model and Fingerprints by DFO Solution

The testing material was passed slowly through the DFO solution. After drying, the testing material was developed at 110°C for 10 min. The DFO solution was prepared by dissolving 50 mg 1,8-Diazafluoren-9-on (Fluka, Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany) in 2 mL glacial acetic acid and 4 mL methyl alcohol. This solution is filled up to 100 mL with HFE 7100 (3M Deutschland GmbH, Neuss, Germany).

Whitening Model and Fingerprints by Acetone Washing

For whitening, the model prints were dipped for some seconds in about 60 mL of acetone. If the whitening effect deteriorated, the acetone needed to be changed.

Whitening Model and Fingerprints with Solutions of the Testing Compounds

For whitening, the model prints were dipped for some seconds in about 60 mL of the solution of the testing compound. For the screening experiments, the solutions were made on the basis of petroleum ether and about 1 g of the testing compound. If they had a bad solubility in petroleum ether, they were dissolved first in some ethyl alcohol and then filled up with petroleum ether (see Fig. 3). For the later experiments with single compounds and mixtures, the solution was prepared in the same way but with the concentrations shown there.

Whitening Model and Fingerprints with the Optimized Solutions of Mixture 3 ("G3")

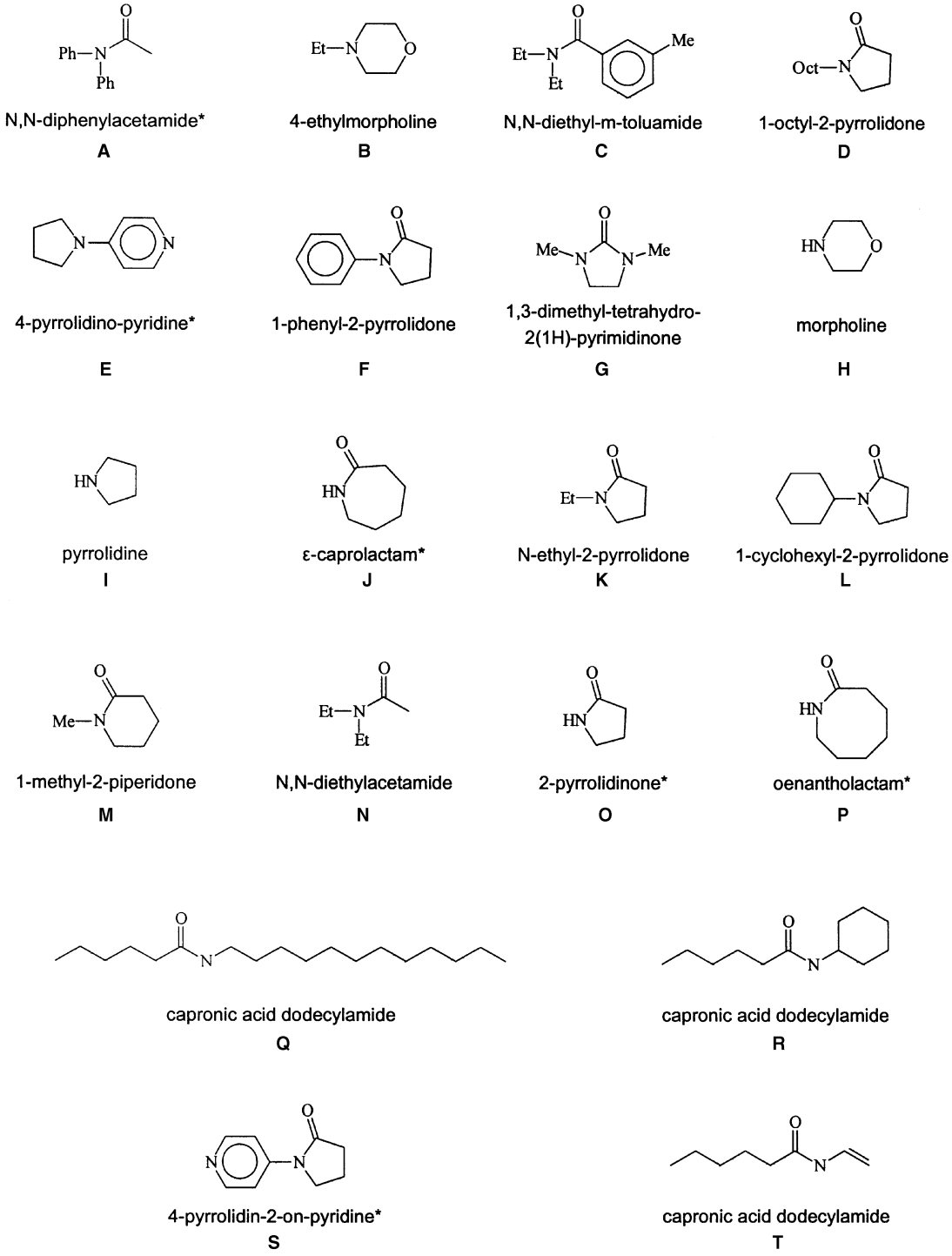
The testing material was passed slowly through the solution of G3, like the application of NPB. The optimized solution G3 was prepared as follows:

1.85 g (12.5 mmol) 4-pyrrolidino-pyridine (**E**), 1.59 g (12.5 mmol) oenantholactam (**P**), 2.47 g (12.5 mmol) 1-octyl-2-pyrrolidone (**D**), and 2.10 g (12.5 mmol) 1-cyclohexyl-pyrrolidone (**L**) were mixed and dissolved carefully in ethyl alcohol until a homogenous, clear solution was achieved, and was filled up to 1000 mL with petroleum ether. One liter of solution is projected for more then 6 m^2 of thermal paper. This is equivalent to about 100 DIN A4 sheets or 75 m of bills with a width of 8 cm.

Whitening Model and Fingerprints with the Solutions of Mixture 3 ("G3N") Containing Ninhydrin

The testing material was passed slowly through the solution of G3N, like the application of NPB. The solution G3N was preapared as follows:

0.3 g (1.7 mmol) ninhydrin (33.7 mM), 93 mg (0.6 mol) 4-pyrrolidino-pyridine (**E**) (12.5 mM), 79 mg (0.6 mol) oenantholactam (**P**) (12.5 mM), 123 mg (0.6 mol) 1-octyl-2-pyrrolidone (**D**) (12.5 mM), and 105 mg (0.6 mol) 1-cyclo-hexyl-pyrrolidone (**L**) (12.5 mM) were mixed and dissolved carefully in ethyl alcohol until a homogenous, clear solution was achieved, and was filled up to 50 mL with petroleum ether. Through this, the solution became



* is soluble in petroleum ether only under addition of ethyl alcohol as solvent promoter

FIG. 3—*Screened compounds.*

dull and a dark blue second phase sediment occured. The testing material is treated only by the petroleum ether phase.

Evaluation of the Experiments

The evaluation was carried out largely visually by two persons. For documentation, the testing material strips were placed on DIN A4 cards and documented by a desk scanner.

The fluorescence of the DFO-treated test material and fingerprints were detected by a VSC 5000 (Foster & Freeman [Europe] GmbH, Bad Wurzach, Germany) of the document section.

Results and Discussion

After the described initial experiments, more compounds (Fig. 3) were tested. All tested compounds had low volatility and had

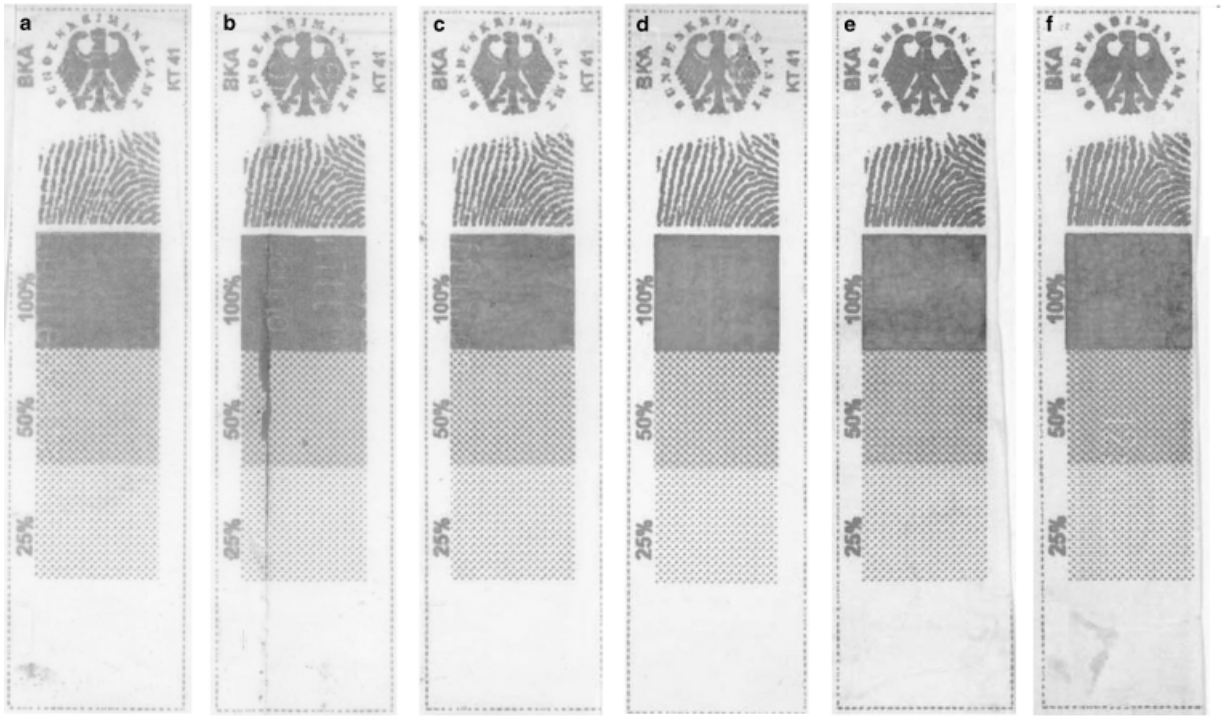


FIG. 4—*(a–f) Test model on thermal paper treatment with ninhydrin petroleum ether and difference after treatment.*

amine and/or amide structures. Most of them were soluble in petroleum ether (in the used range of 1 g in 40–60 mL petroleum ether) or on adding some ethyl alcohol as a solubility promoter.

On application on various thermal papers, oenantholactam (**P**), 1-octyl-2-pyrrolidone (**D**), 1-cyclohexyl-pyrrolidone (**L**), and 4-pyrrolidino-pyridine (**E**) showed the best results in whitening and increasing the contrast of the test prints of all the compounds listed in Fig. 3. Through the application of 4-pyrrolidino-pyridine (**E**), the test prints on most of the used thermal papers showed a color change from violet to blue-violet and the prints appeared

TABLE 1—*Experiment with different concentrations.*

Testing Material	Thermal Fax-Paper			Thermal Paper of Aldi			Thermal Paper of Walmart			Thermal Paper of Aral			Thermal Paper of Real			Thermal Paper of DB			White Copy Paper			Filter Paper			Total
Solution \ After Days:	0	2	7	0	2	7	0	2	7	0	2	7	0	2	7	0	2	7	0	2	7	0	2	7	
100 mM **E**																									22
100 mM **P**																									5
100 mM **D**																									5
100 mM **L**																									5
Mixing 1 50 mM **D**, 50 mM **E**, 50 mM **L**, 50 mM **P**																									2
Mixing 2 25 mM **D**, 25 mM **E**, 25 mM **L**, 25 mM **P**																									20
Mixing 3 12.5 mM **D**, 12.5 mM **E**, 12.5 mM **L**, 12.5 mM **P**																									21
Mixing 4 33 mM **D**, 33 mM **L**, 33 mM **P**																									4
Mixing 5 16.5 mM **D**, 16.5 mM **L**, 16.5 mM **P**																									6
Mixing 6 16.5 mM **D**, 49.5 mM **E**, 16.5 mM **L**, 16.5 mM **P**																									10

Legend: = very good whitening.

= best result.

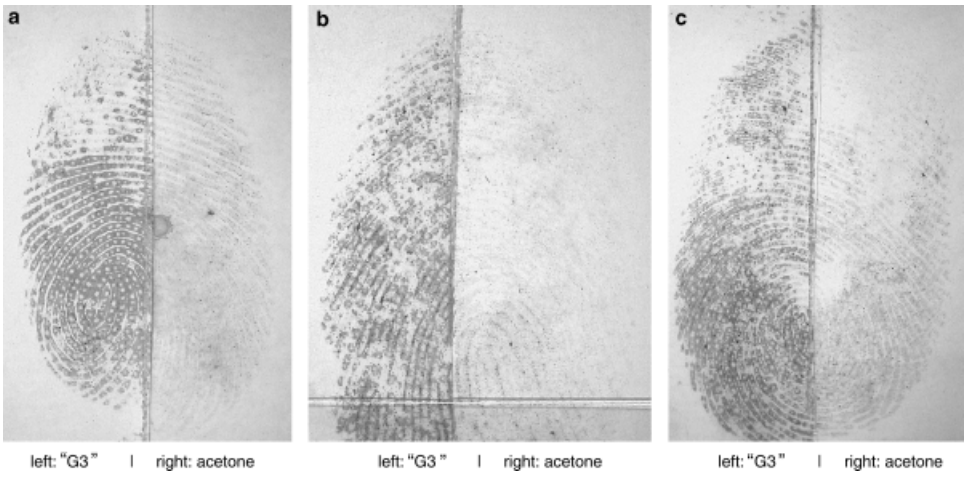


FIG. 5—*(a–c) Real fingerprints on thermal paper after ninhydrin petroleum ether treatment and comparison after treatment of mixture "G3" with acetone.*

particularly sharp and colorful. The background attained some yellowish coloring, which increased on increasing the concentration of compound **E**.

More experiments with these four compounds (**D**, **E**, **L**, **P**) also showed a successful application on thermal papers treated with DFO. The test prints showed DFO fluorescence after dipping in the solutions of compounds **D**, **E**, **L**, **P** both on thermal paper and on white copy paper.

The whitening also took place in the sequences DFO–NPB whitening and DFO whitening–NPB whitening with solutions of all four compounds **D**, **E**, **L**, **P**. No disturbances in the DFO and NPB reaction were observed.

In experiments with solutions of the four compounds **D**, **E**, **L**, **P** in different concentrations (1, 10, 50, 100, 200 mM) the concentration of 100 mM showed the best results among of all the tested thermal papers (Fig. 4*a–d*). On some papers, the whitening occured at 50 mM and on other paper at 200 mM.

To create a dependable whitening and contrast amplification on a maximum number of different thermal papers and to reduce the chemical exposure for the papers treated, we carried out experiments with mixtures of the four compounds **D**, **E**, **L**, **P** (Table 1). As shown in Table 1, the 100 mM solution of 4-pyrrolidino-pyridine (**E**) as well as the solution of mixture 2 and mixture 3 produced the best results in whitening and contrast amplification of the tested solution. On considering of chemical exposure, mixture 3 ("G3"), containing 12.5 mmol 4-pyrrolidino-pyridin (**E**), 12.5 mmol oenantholactam (**P**), 12.5 mmol 1-octyl-2-pyrrolidone (**D**), and 12.5 mmol 1-cyclohexyl-pyrrolidone (**L**), is ideal for practical use. (Fig. 1*e*). In application, the solution of mixture 3 ("G3") is used for NPB dipping. Whitening starts during the dipping itself and usually persists for a week, often even for months, depending on the thermal paper.

Additional experiments showed that, although the solution is used up in quantity, it does not lose its ability of whitening and contrast amplification through repeated use. There is no difference between papers dipped first and papers dipped later. Even a 3-month-old, used solution of mixture 3 ("G3") shows the same results as a freshly made and unused solution (Fig. 4*e–f*).

In comparison with acetone washing, the fingerprints appeared in sharper and higher contrast (Figs. 5*a–c* and 6*a–c*) and ninhydrin-treated prints showed a color change to blue. In addition, ball-point inks did not bleed off.

As far as consumption is concerned, 10 times more acetone is needed than a solution of mixture 3 ("G3") for the same amount of thermal paper.

For the development of mixture 3 ("G3") we tried to incorporate the ninhydrin treatment into a one-step application (Mixture

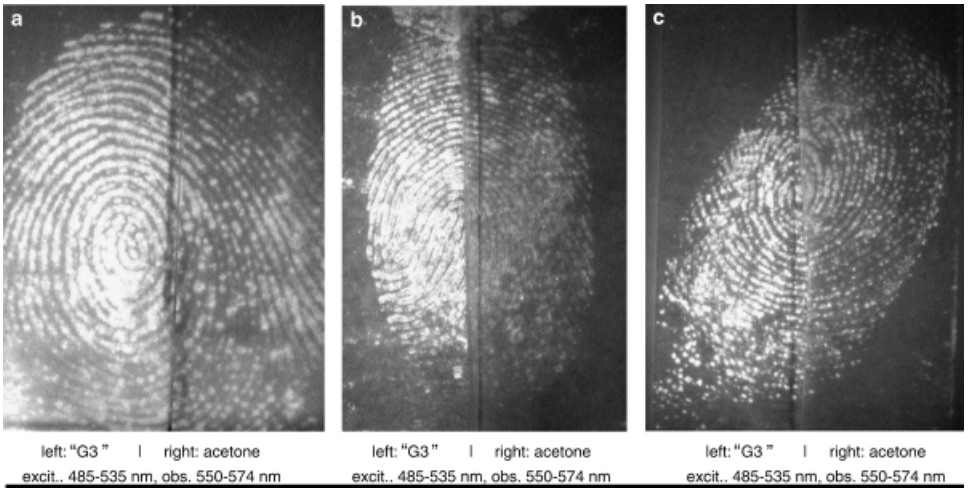


FIG. 6—*(a–c) Real fingerprints on thermal paper after 1,8-diazafluoren-9-one treatment and comparison after treatment of mixture "G3" with acetone.*

3N/"G3N"). For this, the four compounds of mixture 3 and ethyl alcohol were mixed with the addition of ninhydrin. On adding petroleum ether, a second phase sediment occurred, but the petroleum ether phase was used for application. On application of this solution on thermal paper, fingerprints were developed, but the quality was not as good as with the use of the two-step application (first NPB, second G3) because of the lack of sharpness. The solution presented closed a gap in fingerprint detection on thermal paper, particularly in those cases in which the blackening obstructs the identification process. The application yields a good to very good contrast amplification on several thermal papers. This is also observed on normal paper (e.g., white copy paper). Because of the differences in the thermal paper used, the quality and durability of the whitening effect may vary. The photographic documentation should therefore be carried out within 2–3 days after application.

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