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Chemical Development of Latent Fingerprints: 1,2-Indanedione Has Come of Age

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ABSTRACT: The performance of 1,2-indanedione as a latent fingerprint reagent on some types of paper was found to exceed that of DFO, the leading fluorogenic fingerprint reagent. It even exceeds the performance of the sequence, DFO, followed by ninhydrin. No new prints could be observed when ninhydrin was applied after indanedione. On a large number of actual exhibits (used checks) indanedione developed 46% more identifiable prints than the sequence DFO-ninhydrin.

A standard procedure for fingerprint development by indanedione is proposed. Best results are obtained with a 0.2% indanedione solution in HFE7100 solvent containing 7% ethyl acetate, but no acetic acid. It can be recommended to start using 1,2-indanedione, which is already commercially available, in actual fingerprint casework.

KEYWORDS: forensic science, fingerprint development, paper, 1,2-indanedione, 1,8-diazafluorene-9-one, ninhydrin, latent, criminalistics

Since the discovery, in 1990, of the fluorogenic reaction of 1,8-diazafluorene-9-one (DFO) with amino acids (1,2), its application has become the first stage in chemical visualization of latent fingerprints on paper by many forensic science laboratories (3,4). Seven years later, Joullie, Cantu, and their coworkers discovered that 1,2-indanedione (Fig. 1), can also be used to visualize latent prints by direct fluorogenic reaction (5,6). Due to its potential advantages over DFO, indanedione has recently gained attention by a number of research groups, which started to explore its properties, focusing on its sensitivity, solubility, stability, and cost (7–9). The preliminary results were promising but more extensive experiments were required in order to introduce it to actual fingerprint casework.

In the first part of this study, the working conditions with indanedione were optimized in regards to factors such as solvents, concentration, pH, temperature, and humidity. In the second part, the performance of indanedione under these optimal working conditions was compared with that of DFO and with DFO followed by ninhydrin.

Experimental

Indanedione was synthesized in the Casali Institute of Applied Chemistry according to the protocol suggested by Cava et al. (10). DFO was synthesized by this group according to Druey and Schmidt (11).

Optimization of Working Conditions

Latent Fingerprints—Controlled fingerprints were tested in this study. In some of the experiments, fingerprints on paper were divided in half, each half was treated differently, and the two halves were compared. In other experiments, depletion prints were placed on paper and the number of identifiable fingerprints was compared. Depletion prints are deposited by placing a finger on the surface several times consecutively; hence the last fingerprint consists of less sweat than the first fingerprint. Fingerprints on real exhibits were also tested.

Mode of Application—Papers with fingerprints placed on them were immersed in the working solution and, after they fully dried, were placed in an oven for 20 min. DFO-treated paper was developed in a dry oven set at 100°C (3). After optimizing the humidity and temperature conditions for indanedione, indanedione treated paper was placed in a humidity chamber with 60% relative humidity and a temperature of 100°C.

Solvents and Concentration—Like ninhydrin and DFO, it is necessary to dissolve indanedione first in a small volume of a relatively polar solvent and then dilute it with a solvent of low polarity. Initial solvents that were tried in this study were: methyl alcohol, ethyl alcohol, isopropyl alcohol, diethyl ether, acetone, and ethyl acetate. Two solvents that have previously shown promise, Vertrel XF and HFE7100 (12,13), were tested as main carriers, to replace the banned CFC113.

Both carrier solvents are nonpolar and therefore do not dissolve ink, have a "zero" ozone depletion potential, and were originally developed to replace CFC as cleaning agents. Vertrel XF is a hydrofluorocarbon with a structure $CF_3CHFCHFCF_2CF_3$. Its boiling point is 55°C and its TLV (threshold limit value—defines the upper limit of exposure allowed for an eight hour workday) is 200 ppm. HFE7100 is a mixture of two hydrofluoroethers: 50 to 70% methyl-nonafluoroisobutyl-ether, $(CF_3)_2CFCF_2OCH_3$ and 30 to 50% methyl-nonafluorobutyl-ether, $CH_3OCF_2CF_2CF_2CF_3$. Its boiling point is 60°C and its TLV is 750 ppm. Final concentrations of indanedione varied from 0.01% to 0.5% (w/v).

Influence of pH—The reaction of indanedione in an acidic solution (as recommended for DFO and ninhydrin) with fingerprints was examined on various types of known paper. The only property of the paper that affected the quality of the fingerprints was the pH. The paper pH was measured by pressing a wet nonbleeding pH indicator strip down to the paper for 10 min. This method

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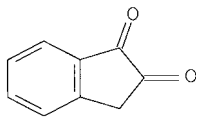


FIG. 1—*1,2-indanedione.*

proved reliable, since the measurements matched with the manufacturer's data.

Acidic and neutral formulations of indanedione were tried on both acidic and neutral paper. Fingerprints were deposited on both types of paper. Half of each paper was developed with an indanedione solution containing 1% acetic acid and half with a solution without acetic acid. The quality of the fingerprints developed and the background fluorescence was compared.

Temperature and Humidity—Exhibits that were processed with indanedione were developed under varying temperature and humidity conditions, the temperature ranging from 40 to 100°C and the relative humidity from 0 to 80%. The exhibits were placed for three days in the dark at room temperature before searching for fingerprints.

Solution Stability—The clarity and fluorescence of fingerprints developed with indanedione working solutions with a number of initial solvents was examined. Alcoholic solvents (methanol, ethanol, and isopropanol), and nonalcoholic solvents (diethyl ether, acetone, and ethyl acetate) were used. Fingerprints were developed with the various solutions when the solutions were fresh and after one week, one month, and two months. After one month the ethyl acetate solution was the only solution that did not lose effectiveness.

Fingerprint Observation—Illuminating the developed exhibits with a Rofin Polilight at 530 nm and viewing through an orange 549 nm cutoff filter revealed luminescent fingerprints.

Optimal Working Conditions for Indanedione—Best results were obtained with a 0.2% indanedione solution in HFE7100 solvent (12,13), containing 7% ethyl acetate. Indanedione (2 g) was dissolved in ethyl acetate (70 mL) and HFE7100 was added to a final volume of 11. It was found that acetic acid, which is used in DFO and ninhydrin solutions, not only did not improve the results but it had a detrimental effect on the clarity of the prints. Thus, the recommended formulation does not contain any acetic acid. Optimal development conditions were found to be 20 min at 100°C and 60% relative humidity.

Comparison with DFO

The performance of the two reagents was compared not on controlled fingerprints, as in the previous chapter, but on a large number of real exhibits. From one of the major Israeli banks, we received 1000 used checks. The checks were processed for fingerprints, 500 of them with the optimized indanedione working solution and 500 with DFO (PSDB formulation (14), 0.025%, 20 min at 100°C; the best formulation of DFO is still based on CFC113, so the comparison was done with this solution). Luminescent impressions of latent fingerprints were observed as described before, and the identifiable prints in each group were counted. Then all the checks in both groups were immersed in ninhydrin solution (14) and new identifiable prints were counted.

Results

After indanedione treatment, two hundred and nineteen identifiable prints developed on 150 out of 500 checks. After DFO treatment, 146 identifiable prints developed on 106 out of 500 checks.

After ninhydrin treatment (after indanedione or DFO), while four new prints developed on four checks initially processed with DFO, two of whom had on them other fingerprints developed in the DFO stage, none developed on indanedione treated checks.

Indanedione developed 50% more fingerprints than DFO on 41% more checks. Indanedione developed 46% more fingerprints than the DFO-ninhydrin sequence on 39% more checks.

Discussion

Over the last decade, DFO has become a universal reagent for latent fingerprint visualization. It is available, efficient and easy to use, although it does require fluorescence photography. The search for either new reagents or new carriers has become a necessity since the ban on the solvent CFC113 (due to its adverse effect on the ozone layer (11)), in which DFO gives the best results.

In the evaluation process of new analytical reagents one must refer to two types of sensitivity. The first is the reaction rate: more sensitive reagents react faster with their substrates. The second is the ease of detection, which is expressed in terms of a more intense color (or fluorescence) of the reaction product. These two factors do not necessarily coincide. Thus, the main advantage of DFO over ninhydrin is the sensitivity of the second type. It develops more fingerprints that are easier to view and examine. However, the reaction of DFO with amino acids, its main substrate in fingerprint deposits, is slower than that of ninhydrin. This is the most plausible explanation for the observation that ninhydrin can still develop new fingerprints after they have initially been treated with the "more sensitive" DFO. Ninhydrin can still react because the reaction with DFO did not go to completion.

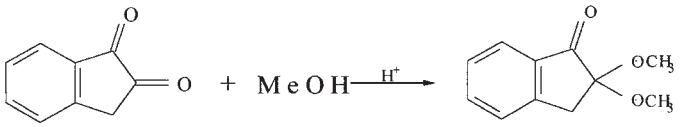
This statement is supported by this group's observation that when latent fingerprints are treated by a solution containing a mixture of DFO and ninhydrin, both in working concentrations, only ninhydrin prints develop. However, in a solution containing indanedione and ninhydrin, both colored and fluorescing fingerprints developed, but are not as intense as those obtained with solutions of each reagent separately.

Indanedione apparently enjoys both types of sensitivity. It reacts faster than DFO and hence, no new prints develop after subsequent treatment with ninhydrin and it also develops more identifiable prints than DFO.

In developing working solutions for DFO and ninhydrin, acid was added to the solutions. The reason for this was the apparent alkalinity of the paper and the need for an acidic environment for the reaction with the amino acids. All papers that we tested were either acidic or neutral. This fact caused us to reconsider the need for acid in the working solution. However, we found that indanedione gave better results on both acidic and neutral paper in the absence of acetic acid.

Although alcohols (methanol, ethanol, and isopropanol) are effective solvents for initial dissolution of indanedione, it is not recommended to use them since the alcohol containing solutions are unstable. We assume that the rapid deterioration is due to the formation of ketals (Fig. 2) upon reaction between indanedione and the alcohol (9,15). Already in 1912 Perkin (16) observed that indanedione changes color when dissolved in alcohols and he concluded that a reaction occurred.

Indanedione has recently become commercially available.



1,2-indanedione

2,2-dimethylketal of 1,2-indanedione

FIG. 2—*Reaction between 1,2-indanedione and methanol.*

Conclusion

It seems that 1,2-indanedione has successfully passed the "acceptance tests" for use in casework as a fingerprint development reagent on certain types of paper exhibits. It will be adopted for use in our lab and in a short time, results from use in casework will be reported.

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