



I,2-IND

BVDA

CATALOGUE NO. B-78100

product information**BVDA INTERNATIONAL**

PO BOX 2323 2002 CH HAARLEM HOLLAND

TEL +31 (23) 5424708 FAX +31 (23) 5322358

EMAIL INFO@BVDA.NL WWW.BVDA.COM

History

1,2-Indanediones were first synthesized as intermediates for the preparation of substituted ninhydrins (e.g., 5-methylthioninhydrin) by Professor Madeleine Joullié and her graduate students, Dr. Diane Hauze and Dr. Olga Petrovskaia, from the University of Pennsylvania (UPenn). During the evaluation of the compounds at the U.S. Secret Service (USSS) by Dr. Tony Cantu and Robert Ramotowski, it was discovered that these compounds were also capable of visualizing latent prints.

Indanediones versus DFO

A range of substituted indanediones were made by UPenn and tested by the USSS [1]. Dr. Joseph Almog and researchers from the Israel National Police also synthesized and evaluated a considerable number of indanediones [2]. Australian researchers compared 1,2-indanedione and 5,6-dimethoxy-1,2-indanedione to ninhydrin and DFO [3]. Wiesner et al. evaluated the performance of 1,2-indanedione (2 g/l in HFE-7100 solvent containing 7% ethyl acetate) on used checks [5].

These research papers concluded that indanediones can visualize latent prints as well as or even better than DFO. Like DFO, the indanediones do not produce strongly colored initial print development (typically a pale pink color), but they do produce strongly fluorescent detail when excited with green light.

Unsubstituted indanedione (1,2-indanedione) was shown to produce fluorescence comparable to DFO. Its ease of preparation, lower cost, and good solubility caused the Israel National Police to conclude that this reagent might "soon become a practical fingerprint reagent."

The Australian study "confirmed that 1,2-indanedione and 5,6-dimethoxy-1,2-indanedione may offer less expensive alternatives to DFO while still developing similar quality prints."

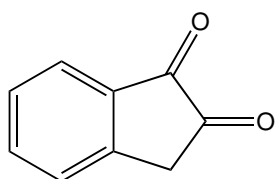
Wiesner et al. later found [5] that 1,2-indanedione developed 46% more identifiable fingerprints than DFO on actual exhibits (500 used checks) and concluded that "It can be recommended to start using 1,2-indanedione, which is already commercially available, in actual fingerprint work."

English research [6] in which several DFO formulations (DFO in a concentration of 0.25 g/l or less) and a 0.23 g/l 1,2-indanedione formulation were compared found that their IND formulation developed identifiable fingerprints in less cases than their best DFO formulation (54.2 compared to 62.5% of the cases).

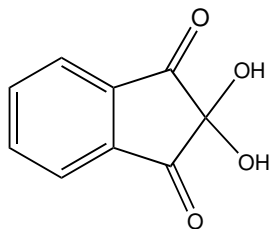
The formula published by Wiesner [5] was validated and published by the FBI and the Florida Department of Law Enforcement [7] to fulfill "the Daubert requirement that scientific processes be validated and subjected to peer review."

A number of substituted indanediones (e.g., 5-methoxy and 5,6-dimethoxy) gave superior fluorescence compared to DFO (especially the 5,6-dimethoxy-1,2-indanedione). Unfortunately, synthesis of these substituted indanediones is somewhat complex and makes their production rather costly. In addition, 5,6-dimethoxy-1,2-indanedione was found to suffer from low solubility in the preferred apolar solvents (e.g., petroleum ether) used in most fingerprint laboratories.

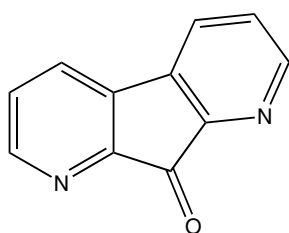
The testing of 1,2-indanedione by groups around the world has shown that it can be used as a replacement for DFO. However, working solutions (in the currently recommended apolar solvents) do not appear to be stable indefinitely. Indanedione molecules will eventually interact to form compounds that will not visualize latent prints. Therefore, working solutions should be made up whenever needed and should not be kept for extended periods of time (i.e., no more than several weeks). However, in the powder form the compound is completely stable.



Chemical structure of
1,2-IND (1,2-indanedione)



Chemical structure of
ninhydrin



Chemical structure of
DFO

Like ninhydrin, latent prints visualized with indanediones can be treated with zinc chloride to slow the fading of visible and luminescent detail. In general, an increase in fluorescence is also observed after treatment with zinc chloride. Cooling in liquid nitrogen, after zinc treatment, was found to further increase the fluorescence [3].

Developing prints on recycled paper

On a number of low quality papers (like newspapers, cardboard, and recycled paper in general) we found that indanediones did not develop fingerprints, where ninhydrin and DFO did. In general, however, the UK Police Scientific Development Branch (PSDB) concluded after experiments with a range of papers that in practice there is little difference between DFO and I,2-indanedione.

Developing prints on thermal paper

Research by Jon Stimac [8] of the Oregon State Police showed that the HFE-7100 formulation published by Wiesner et al. [5] of IND can be used on thermal papers. Thermal paper (fax paper) is used extensively for printed receipts in automatic teller machines (ATM) and point-of-sale registers. The active layer in the paper is very susceptible (turns dark or the print dissolves) for polar solvents like acetone, ethanol and acetic acid. This makes use of DFO and ninhydrin on these papers problematic. For this reason development of prints on thermal paper is best done at room temperature (excessive heat will discolor the paper also).

Formulations

The following working solutions were developed by the PSDB:

| | | | |
|--------|-------------------------------|---------|-------------------------------|
| 0.2 g | I,2-indanedione | 0.25 g | I,2-indanedione* |
| 8 mL | glacial acetic acid (99-100%) | 10 mL | glacial acetic acid (99-100%) |
| 72 mL | ethyl acetate | 90 mL | ethyl acetate |
| 800 mL | petroleumether | 900 mL | HFE-7100 |
| ----- | | ----- | |
| 880 ml | working solution | 1000 mL | working solution |

* 1 g recommended by Wallace and Roux [9a, 9b]

Note that solvents like pentane and heptane can be substituted for petroleum ether. The I,2-indanedione should first be added to the mixture of ethyl acetate and acetic acid and allowed to dissolve completely. The petroleum ether (or HFE 7100) should then be slowly added to the mixture. HFE 7100 is the current recommended replacement solvent for Freon (1,1,2-trichlorotrifluoroethane, also known as CFC-113, Frigen, Arklone, and Fluorisol).

Note also that methanol or ethanol should not be used in the working solutions. These solutions are not stable over more than a few weeks [4, 5].

Store the solution in a dark brown glass bottle, in the dark. From the chemical literature it is known that I,2-indanediones are prone to photochemical reactions upon exposure to sunlight.

Since most groups that have studied I,2-indanedione found higher concentrations (up to 5 grams per liter) to give stronger fluorescing prints, we recommend the following modified solution, based on the petroleum ether formulation of the PSDB:

| | |
|---------|---------------------|
| 1 g | I,2-indanedione |
| 10 mL | glacial acetic acid |
| 90 mL | ethyl acetate |
| 900 mL | petroleumether |
| ----- | |
| 1000 mL | working solution |



The formulation used by Wiesner et al. [5] does not contain acetic acid. They found that acetic acid did not improve the results, but had a detrimental effect on the clarity of the prints in their HFE-7100 formulation:

| | |
|---------|------------------|
| 2 g | I,2-indanedione |
| 70 mL | ethyl acetate |
| 930 mL | HFE-7100 |
| ----- | |
| 1000 mL | working solution |

Developing and viewing the prints

The best method for developing prints on documents with these compounds is still being investigated. For I,2-indanedione, most groups that did research in this area used a humidity oven (10-20 minutes at about 100°C, with approximately 60% relative humidity). At BVDA, we used only dry heat. However, we found that latent prints continued to develop on samples when left overnight (and afterwards) at ambient laboratory conditions.

The PSDB reported optimum development when documents were heated for 10 minutes at 100° C (no humidification). Australian researchers [3] preferred a heat press (15 seconds at about 120° C) or 160° C for 10 seconds [9a, 9b] to dry heating for 20 minutes at 100° C.

The validation study of the FBI and Florida Department of Law Enforcement [7] concluded that best results were obtained by heating for 2-5 minutes in a photographic mounting-press at 100° C (a similar procedure as used by the Australians [3]) compared to heating in an oven at 100° C for 20 minutes.

Prints developed with I,2-indanedione will fluoresce under green light (optimum about 530 nm), similar to DFO. Optimum viewing and photographing is done with dark orange glasses/filters (cut on point 570-590 nm).

Sensitivity to light

Research has shown that developed prints are sensitive to daylight. Decreasing fluorescence intensity was observed when prints were not stored in the dark. When stored in the dark, prints retain their fluorescent properties for a long time.

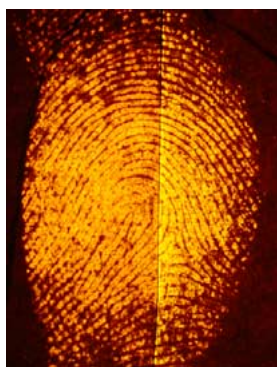
The green light used to view and photograph the fluorescence appears to cause only a temporary decrease in fluorescence intensity, and only after extended periods of exposure (several hours). The fluorescence returned after storage in the dark overnight, according to the PSDB.

Procedure for preparation of the zinc chloride solution

For the treatment with zinc chloride, we developed the following non-CFC formulation, which is very reliable and stable (we have stored and used solutions that were several years old, without any problem). In Europe, this solution can be obtained from us:

Dissolve 30 grams of zinc chloride in a mixture of 500 mL methyl-tert-butylether (MTBE) and 20 mL of anhydrous ethanol (98% or more) using a 1 liter erlenmeyer flask, a magnetic stirring bar, and a magnetic stirrer, in a fume hood. It will take 30-60 minutes to dissolve completely.

After it is fully dissolved, add 10 mL of glacial acetic acid (99-100%) and dilute with 500 mL of a hydrocarbon solvent (petroleum ether, pentane, heptane). Store in a brown glass bottle.



Comparison of the fluorescence of DFO (left) and 1,2-IND (green light/dark orange filter).



Procedure for treatment with zinc chloride

Zinc chloride treatment of prints on paper, developed with 1,2-indanedione, is a very simple procedure. We recommend that a sprayer should be used in a fume hood to apply the zinc chloride. Spray the solution on the article lightly, allow the solvents to evaporate, and then spray the article again if needed. There is, however, no change of color or any other indication that spraying was sufficient as in the case of ninhydrin.

References

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- [9b] Wallace, Christie; Claude, Roux; poster presented at the IAI-conference in St. Louis, August 2004 (to be published).