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TR-08-94
A Comparison of Thenoyl Europium Chelate with Ardrox and Rhodimine 6G for the Fluorescent Detection of Cyanoacrylate Fingerprints

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TECHNICAL REPORT

Submitted by

Canadian Police Research Centre

December 1993

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SUMMARY

Thenoyl Europium Chelate (TEC) is a fluorescent dye that can be used to detect cyanoacrylate developed fingerprints. TEC absorbs ultraviolet light near 350 nm and emits a narrow band at 614 nm. Such ideal spectral features mean that TEC has several advantages over the existing fluorescent stains Ardrox and Rhodamine 6G. This study compares the ability of Ardrox, Rhodamine 6G and TEC, at visualising cyanoacrylate developed fingerprints on a variety of surfaces, in terms of the brightness of print fluorescence, the clarity of the print and the absence of contaminating background fluorescence.

RÉSUMÉ

Le chélate europium-thénoyle (CET) est un colorant fluorescent qui peut servir à déceler des empreintes digitales développées avec du cyanoacrylate. Le CET absorbe la lumière ultraviolette près de 350 nm et émet une bande étroite à 614 nm. Grâce à ces caractéristiques spectrales idéales, le CET présente plusieurs avantages par rapport aux colorants fluorescents actuels comme l'Ardrox et la Rhodamine 6G. Dans la présente étude, on compare la visualisation d'empreintes digitales développées avec du cyanoacrylate obtenue avec l'Ardrox, la Rhodamine 6G et le CET sur diverses surfaces, d'après l'intensité de la fluorescence de l'empreinte, la clarté de l'empreinte et l'absence de contamination par une fluorescence de fond.

INTRODUCTION

Many fluorescent dyes are suitable for the visualisation of cyanoacrylate (CA) developed latent prints, including Gentian Violet [1], Coumarin 540 [1], Rhodamine 6G [2], Ardrox [3], Brilliant Yellow [4], a variety of textile dyes [5], and, more recently, Thenoyl Europium Chelate (TEC) [6,7]. Although all these dyes have different spectral and chemical properties there have been surprisingly few studies published comparing their different abilities to develop fluorescent fingerprints. Kobus *et al.* conducted a study which compared the cyanoacrylate dyes, Gentian Violet and Coumarin 540, on a variety of surfaces [1] and McCarthy recently published a comparison of Ardrox and Rhodamine 6G [8].

TEC is composed of two components, an organic ligand capable of absorbing ultraviolet light, and the europium metal ion, Eu^{3+}. Under ultraviolet excitation the ligand absorbs light energy and transfers it to the europium ion. The europium ion then re-emits its characteristic narrow band (10 nm FWHM) fluorescence at 614 nm.

The objective of this comparison study was to establish whether TEC in practice developed cyanoacrylate treated latents as well as Ardrox and Rhodamine 6G. Fingerprints deposited on different surfaces were treated with the three fluorescent dyes and the results, in photographic form, were sent to RCMP Identification Specialists throughout Canada for evaluation. The survey approach was chosen so that the results of the study would be evaluated by an unbiased group of experts who were kept unaware of the dye used to visualise each individual fingerprint.

EXPERIMENTAL

Sample Preparation

Ten surfaces were selected (aluminum foil, acetate, 'Ziploc' bag, 'Glad' kitchen garbage bag, green garbage bag, 'A&P' grocery bag, hard white plastic, 'Loblaws' grocery bag, black garbage bag, cigarette foil) based upon the difficulty with which fingerprints can be developed on them. They ranged from ideal surfaces such as aluminum foil to extremely difficult ones such as cigarette foil. Since methyl ethyl ketone (MEK), the solvent used to transfer TEC into polycyanoacrylate, can attack some surfaces such as polyvinyl chloride (PVC) and polystyrene, these surfaces were not included in the study.

Print Deposition

Fingers were gently wiped across the forehead and hands rubbed together to ensure even distribution of the sebum over the fingers. Fingerprints were deposited under medium pressure in order for a good quality fingerprint to be deposited each time. It was felt that using high quality prints would enable a fair comparison between techniques as opposed to using weak prints of uneven distribution of material. Each surface sample was divided into three sections and five fingerprints were deposited so that every second print overlapped two sections (see Figure 1).

Cyanoacrylate Development

The samples were placed in the Watkin Vacuum chamber (ETM Industries, Renfrew, Ontario, Canada) and exposed to cyanoacrylate (Loctite 495 Superbonder) for 30 minutes at 0.2 torr and 0% humidity.

Print Visualisation

After CA fuming the samples were cut along the divisions into three separate sections (A, B and C), each section was treated with a different dye. Section A was not treated with the same dye for all ten samples. For example, Ardrox was used to develop section A in 6 samples, section B in 1 and section C in 3. Sections B and C were treated in a similar manner. Each fingerprint was developed until the highest quality print possible was observed using dye solutions recommended in the literature [2,7,9].

TEC

Samples were immersed in a solution containing 0.1g/L of TEC in 22% MEK in water until the highest quality print was observed. The samples were removed from the solution and allowed to dry for about 30 seconds before washing with a solution of 80% methanol in distilled water.

Ardrox

Samples were immersed in a 2% solution of Ardrox in methanol until the highest quality print was observed. The samples were removed and washed under running water and allowed to air dry. Samples were also tested to see if air drying without water washing produced better prints. It was found from these samples that immediate washing gave the best results. In contrast to Fallano [9], washing with 10% acetic acid was found to weaken print fluorescence and in some cases completely removed the Ardrox stain from the print.

Rhodamine 6G

Samples were immersed in a 0.025 g/L Rhodamine 6G solution in methanol (preferred formulation used by the RCMP) until the best quality print was observed. The samples were removed and allowed to air dry before washing in methanol.

Photography

Two sets of photographs were taken. In Series II the sections were reassembled and photographed together with the camera set for automatic exposure so that the brightest print image could be captured (Figure 1). In Series I each of the three sections from each surface were photographed individually to capture the best fingerprint image possible (Figure 2). In addition to Series II an approximate quantative measure of the relative print fluorescence between sections was obtained by recording the different exposure times for each image in Series I. Images were recorded using Kodak Technical Pan Film with a Nikon F3 35mm automatic camera equipped with a Schott KV 550 filter and mounted on a tripod.

For both series of photographs the sections were illuminated with the appropriate excitation light source to achieve maximum print fluorescence. For excitation of TEC and Ardrox, Spectronics Model B1B-150B mercury lamps were used (one lamp directed at each dye) and for excitation of Rhodamine 6G a Spectra-Physics 2035 Argon Ion laser ("all lines") was used. The power output of each light source was measured at the sample surface using a Scientech 3610 Power Meter. The power from the 365 nm mercury line of the lamp was 0.15 W/ cm^2 and the power transmitted through a fibre optic cable of the laser was 1.5 W/ cm^2.

Survey

Copies of the photographs from Series I and II were sent together with an instruction sheet and result tables (see Appendix 1 and 2) to seventeen RCMP Forensic Identification Sections for evaluation. The photographs were labelled according to the surface. Participants were asked to evaluate Series I before seeing Series II to avoid biasing the results (see Discussion).

Scoring

For Series I the respondents were asked to assess the fingerprints according to two criteria: the clarity of the print and the presence of contaminating background fluorescence. They were instructed to use **only** the whole fingerprint from the centre of each section to judge print clarity and to use the total area of each section to judge background. These criteria were defined as follows: (1) print clarity refers to the ability to see clearly the continuous ridge detail throughout the **entire** print, and, (2) background fluorescence refers to contamination of the background by fluorescent dye sticking to the sample surface. It is undesirable **wherever** it appears. To illustrate these factors the sample labelled white plastic was used as an example (see Appendix 1).

After assessing the fingerprints the respondents were asked to score the individual section (A, B and

C) out of a maximum of five marks for print clarity and out of a maximum of five marks for background. A guide to scoring was suggested and the scores were recorded in Table I (see Appendix 1).

For Series II the respondents were asked to choose the section which they felt showed the brightest print fluorescence. They were asked to rank their first, second and third choice in the Table II (see Appendix 2).

RESULTS

Figures 3 and 4 illustrate the results from the Series I photographs which correspond to print clarity and background fluorescence, respectively. The percentage score shown on the vertical axis represents a total score which is arrived at by simply combining the individual scores given for each dye on each different surface by each respondent. In the majority of samples this score is out of a maximum of 230, since each dye could be given a maximum score of 5 and there were 46 respondents.

The horizontal axis identifies the ten surfaces and the score for each dye is represented by a coded bar (TEC-solid bar; Ardrox- hatched bar; Rhodamine 6G-blank bar).

From Figure 3 it is clear that in seven out of the ten samples TEC has been judged to produce prints with a higher quality of ridge detail than either Ardrox or Rhodamine 6G. For the foil sample Ardrox and TEC are judged to be equal whereas for the two remaining samples (acetate and garbage bag) Ardrox was selected over TEC and Rhodamine 6G.

Figure 4 illustrates the total percentage scores for the absence of contaminating background fluorescence for all ten samples. Again for seven of the ten samples TEC has been selected over Rhodamine 6G and Ardrox. For the aluminum foil sample TEC can be considered equal to Ardrox and in the remaining two samples (acetate and glad bag) Rhodamine 6G was selected as giving the clearest background.

The scores generated when the dyes were compared on their ability to produce the brightest print fluorescence are shown in percentage form in Figure 5. A total of 45 officers responded. From Figure 5 it can be seen that TEC was chosen in eight out of ten surfaces to give the brightest print fluorescence and that Rhodamine 6G was chosen in the remaining two samples (acetate and cigarette foil).

Finally a grand score can be derived by adding the scores for all ten surfaces for each of the three criteria: brightness, clarity, and background. This information is shown in the form of pie charts in Figure 6. The overall result from this survey can be summarised from these pie charts and is that TEC produced prints of equal but usually better quality in terms of clarity and background to the existing stains, Ardrox and Rhodamine 6G. However, more importantly, TEC treated prints are significantly brighter than the corresponding prints developed by Ardrox and Rhodamine 6G. This is also illustrated by comparing the images seen in Figure 1 to those of Figure 2. The same sample is shown in both Figures. In Figure 1 the central section (visualised with TEC) has been captured as the brightest image but as can be seen from the images developed in Figure 2 all three sections show excellent quality prints.

DISCUSSION

In theory TEC has several advantages (listed in Table 1) over the existing stains Ardrox and Rhodamine 6G. Such advantages include a narrow emission band in comparison to Ardrox, and a very large Stokes shift and ultraviolet excitation compared to Rhodamine 6G. In practical terms these factors translate into good filtering capability for the blocking of unwanted backgrounds and the use of cheap, portable light sources. However, perhaps TEC's most important advantage is that it is transferred into the interior of the polycyanoacrylate print by the 'carrier' solvent methyl ethyl ketone [7]. We believe this transfer process allows for a large amount of dye to be trapped in the print when the MEK evaporates.

The absolute brightness of a dyed fingerprint is dependent on three factors: (1) the efficiency of the dye in absorbing and re-emitting the light which is called the quantum yield, (2) the power of the exciting light, and, (3) the amount of dye in the print. The quantum yields for Rhodamine 6G and TEC in ethanol are 0.95 and 0.19, respectively [10, 11]. Rhodamine 6G is a laser dye and its quantum yield is extremely high. The quantum yield of TEC inside the CA polymer is unknown.

TEC gives brighter prints than those treated with Rhodamine 6G even though the laser light source used to excite Rhodamine 6G generates ten times the power output compared to the UV lamp. This implies that the amount of dye present in the TEC treated print is appreciably larger than the amount of dye present in the Rhodamine 6G print especially since Rhodamine 6G is known to have a high quantum efficiency. Simply increasing the amount of Rhodamine 6G in solution as a way of acheiving prints of similar brightness to TEC is not the answer. Menzel has discussed the problems of using too high a Rhodamine 6G concentration in the methanol staining solution ..."It was then often necessary to rinse the article with methanol after staining to wash off excess dye from the surface of the article. This rinsing often is detrimental to the fingerprint" [12].

We explain this result by postulating the transfer of TEC into the interior of the CA. Both Ardrox and Rhodamine 6G are applied as methanol solutions which is a solvent that does not chemically attack polycyanoacrylate. Therefore it is reasonable to suggest that Ardrox and Rhodamine 6G are merely adsorbed onto the surface. In contrast MEK penetrates the polymeric CA attracting TEC from the aqueous solution into the print interior. It is well known that the quantum yield increases significantly when dyes are dissolved in rigid environments [13]. Therefore, we believe that the already reasonable quantum yield for TEC will increase when it is transferred into the polymer. It is quite reasonable to believe that both Ardrox and Rhodamine 6G could also be transferred into the polymer using MEK. However, the small Stokes shift of Rhodamine 6G and the broad emission band of Ardrox mean that TEC is still favored in terms of spectral features.

The purpose of this study was to determine how TEC compared to the existing stains. Therefore a major concern in this project was how to achieve a meaningful result without being biased in favour of TEC.

All comparison studies can be seen to be flawed to some extent but we have tried at every step of the process to be fair to all three dyes and as a result the following decisions were made;

1) For the choice of surfaces, a group of nine RCMP Identification officers were asked to suggest surfaces that are either common or problematic.

2) Only good quality fingerprints were used so that each dye would have no excuse for not producing a good quality print.

3) Rather than setting a time limit for immersion of the print in the dye solution, each dye was allowed to develop the best print possible.

4) Since the quality of the print image is just as important as brightness of print fluorescence the samples were photographed in two different configurations in order to evaluate brightness, clarity and background.

5) Rather than judging the results ourselves, photographs were sent to Forensic Identification experts who had no idea which dye they were evaluating from one picture to the next.

6) Finally since TEC generally produced the brightest prints we did not want to bias the group in favour of this dye when they were judging print clarity and background so we asked that they evaluate Series I first before seeing Series II.

CONCLUSION

The theoretical advantages of TEC over Ardrox and Rhodamine 6G have been reinforced by the results of this comparison study. As a consequence of the transfer of TEC into the CA print, TEC produces brighter print fluorescence on the majority of surfaces without compromising clarity or contrast, compared to similar prints developed with Ardrox and Rhodamine 6G.

Following these results the RCMP has undertaken a program to introduce TEC into Forensic Identification Sections throughout Canada and to continue to assess the dye based on casework.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Drs John Watkin and Brian Yamashita for their valuable contribution to this work. In addition we wish to express our gratitude to the many RCMP Identification Specialists who participated in this study.

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Summary of Figures

Table 1: Features of Fluorescent Dyes

Dye	Stokes shift	Emission Band Width	Excitation Source	Transfer into CA
TEC	264 nm	10 nm	U.V.	Yes
Rhodamine 6G	40 nm	40 nm	Laser	No
Ardrox	210 nm	70 nm	U.V.	No

APPENDIX 1: Comparison of Fluorescent Fingerprint Dyes
Evaluation of Series I Photographs

Each sample represents a different surface and has been divided into three sections labelled A, B and C (each section has been treated with a different fluorescent dye). The samples have been treated randomly so section A does not always correspond to one particular dye. Photographs were taken under optimum conditions.

Please assess these fingerprints on the clarity of the print and the presence of contaminating background fluorescence, use **only** the whole fingerprint from the centre of each section to judge print clarity and use the total area of the section to judge background.

Factors to consider when scoring print clarity and background fluorescence; (1) Print Clarity refers to the ability to see clearly the continuous ridge detail throughout the **entire** print,
(2) Background Fluorescence is undesirable **wherever** it appears. It refers to the contamination of the background by fluorescent dye sticking to the sample surface.

To illustrate these factors please consider the sample labelled White Plastic as an example;

Section	Print Clarity	Background Fluorescence
A	Ridge detail quite clear and continuous	No background fluorescence present
B	Ridge detail spotty and difficult to follow	No background fluorescence present
C	Uneven dyeing results in significant loss of ridge detail in upper section	Considerable background

After assessing the fingerprints please score the individual section (A, B or C) out of a maximum of five marks for print clarity and out of a maximum of five marks for background. Please put your scores in Table I. The scoring is shown below;

Score	Print Clarity	Background Fluorescence
5	Excellent	No Background
4	Very good	15% coverage
3	Good	30% coverage
2	Fair	50% coverage
1	Poor	80% coverage
0	Unsatisfactory	Unsatisfactory

Table I:

Surface	Section	Print Clarity	Background
	A		
Aluminum Foil	B		
	C		
	A		
Acetate	B		
	C		
	A		
Ziploc Bag	B		
	C		
	A		
Glad Bag	B		
	C		
	A		
Garbage Bag	B		
	C		
	A		
A&P Bag	B		
	C		
	A		
White Plastic	B		
	C		
	A		
Loblaws Bag	B		
	C		
	A		
Black Bag	B		
	C		
	A		
Cigarette Foil	B		
	C		

APPENDIX 2: Comparison of Fluorescent Fingerprint Dyes
Evaluation of Series II Photographs

Each sample represents a different surface and has been divided into three sections labelled A, B and C where each section has been treated with a different fluorescent dye. The samples have been treated randomly so that section A does not always correspond to one particular dye. The samples were photographed simultaneously using an automatic exposure in order to capture the brightest fingerprint.

Please choose your preferred section based on the brightness of the print fluorescence. All of the dyes have been illuminated with the light source appropriate for their excitation.

Please put your choices in Table II. An example (shown in *italics*) has been given in the first row of the table.

Table II:

Surface	1st choice	2nd choice	3rd choice
Aluminum Foil	*B*	*C*	*A*
Aluminum Foil			
Acetate			
Ziploc Bag			
Glad Bag			
Garbage Bag			
A&P Bag			
White Plastic			
Loblaws Bag			
Black Bag			
Cigarette Foil			

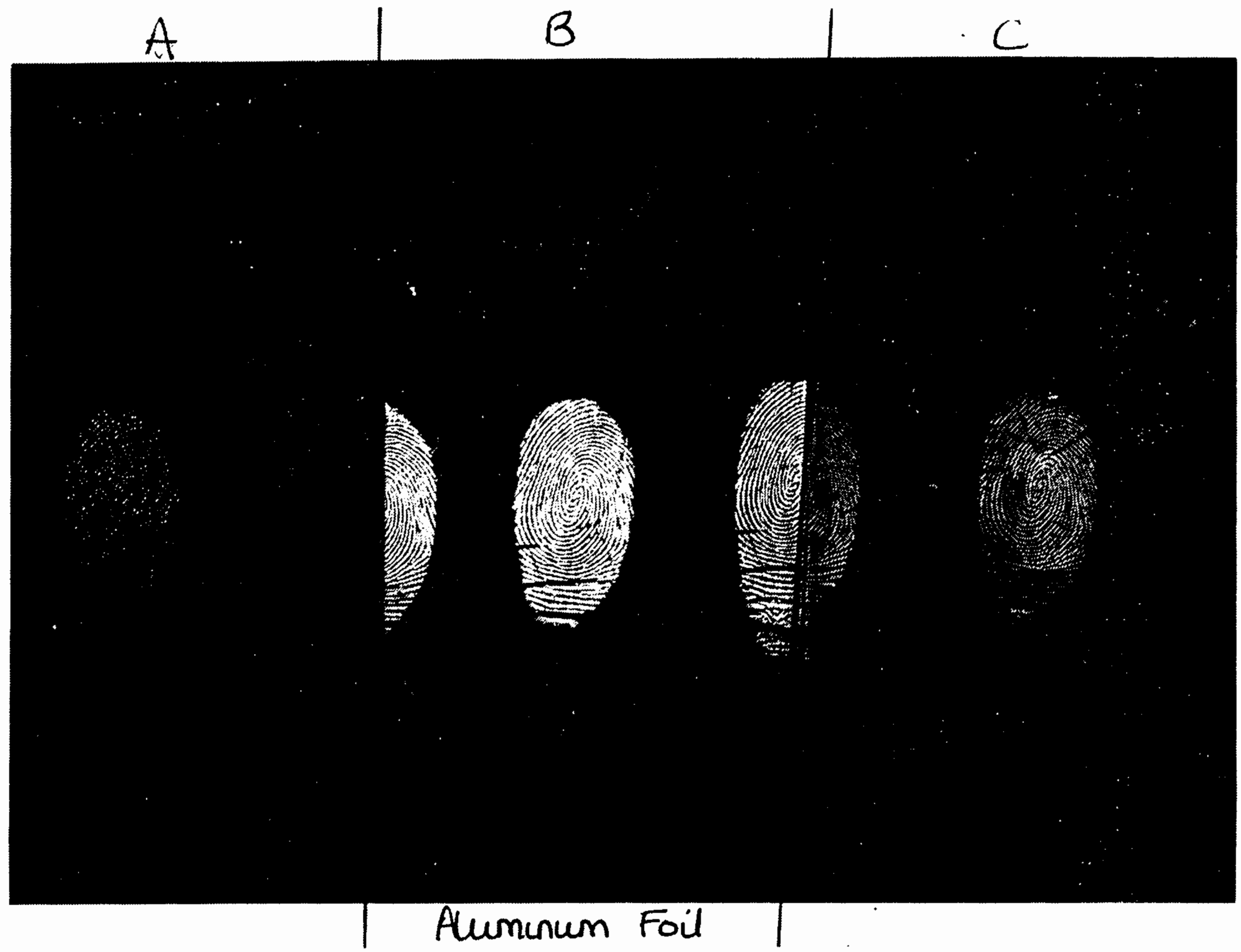

Figure 1 Photograph of aluminum foil sample from Series II. Each section has been treated with a different dye (A: Ardrox; B: TEC; C: Rhodamine 6G).

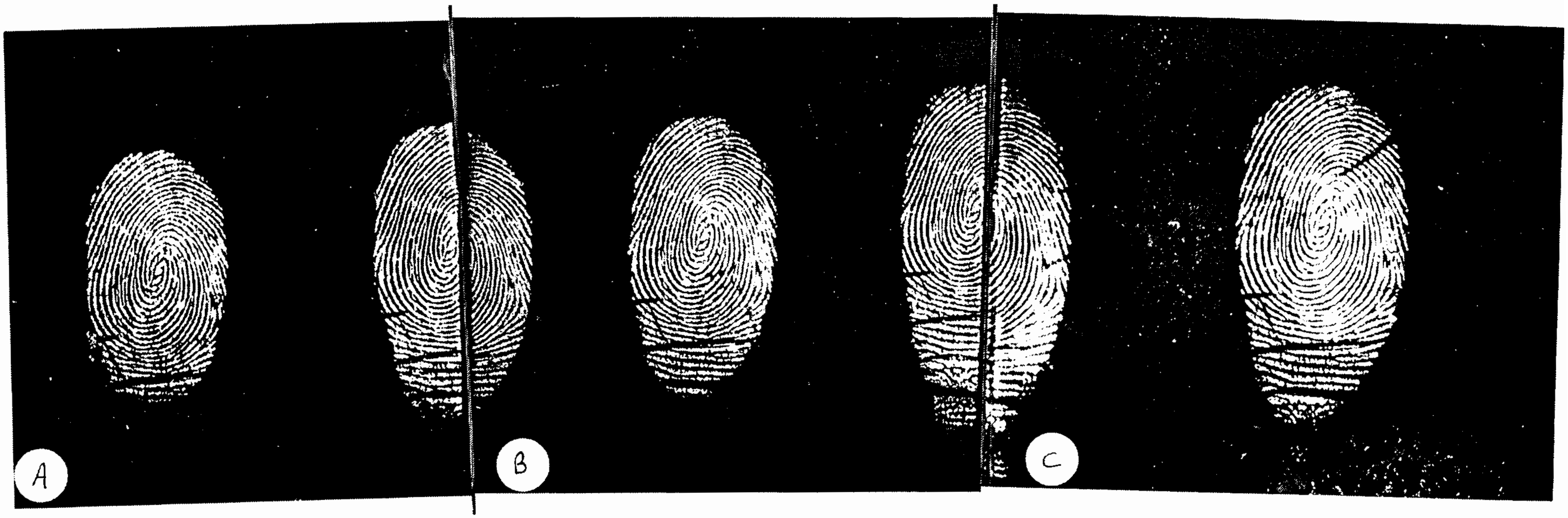

Figure 2 Photographs of the three separate sections of the aluminum foil sample from Series I. The time exposures varied for each section; (a) Ardrox 6s, (b) TEC 3s, and (c) Rhodamine 6G.

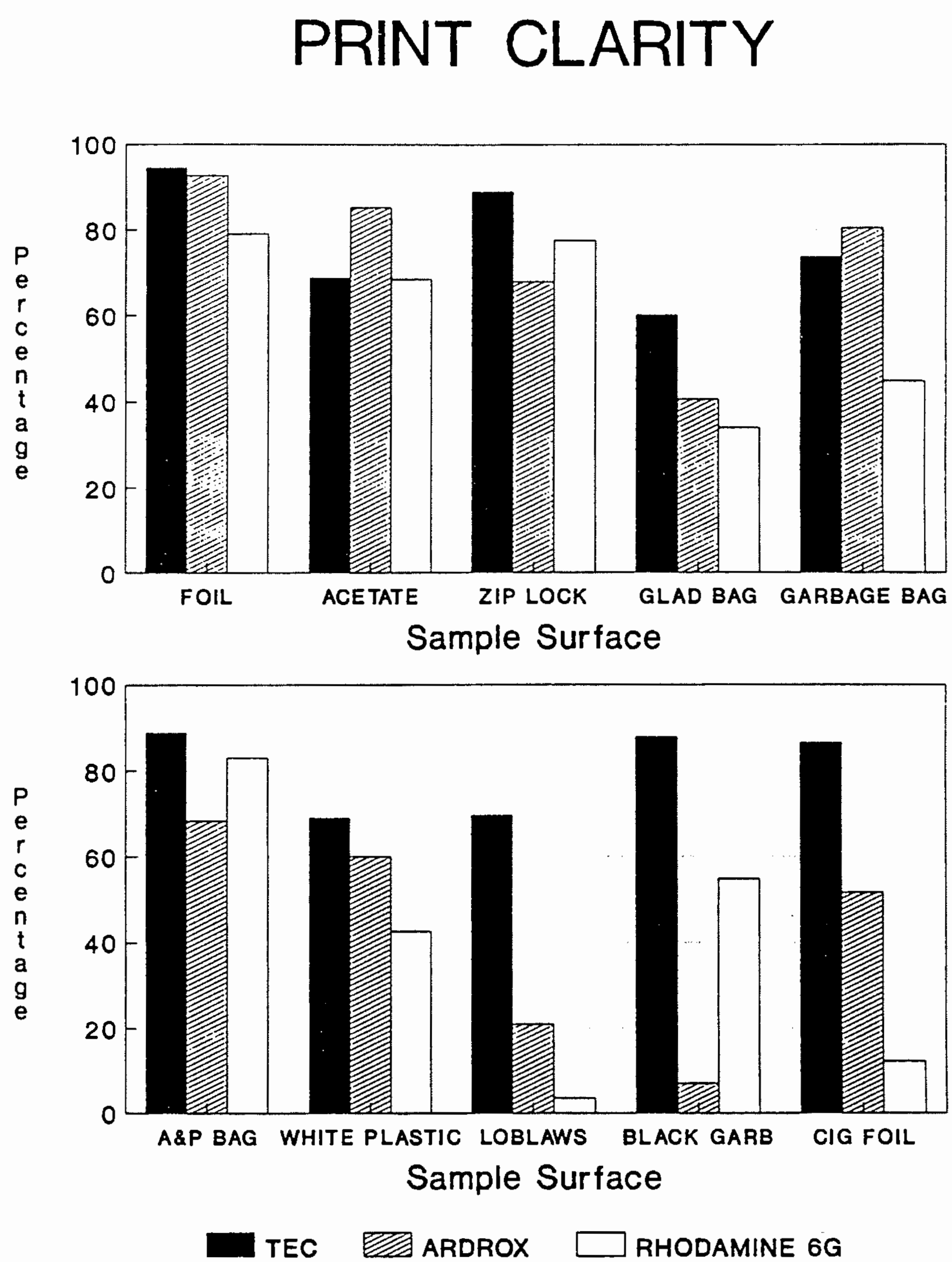

Figure 3 Percentage scores for print clarity for all ten surfaces. TEC (solid), Ardrox (hatched) and Rhodamine 6G (blank).

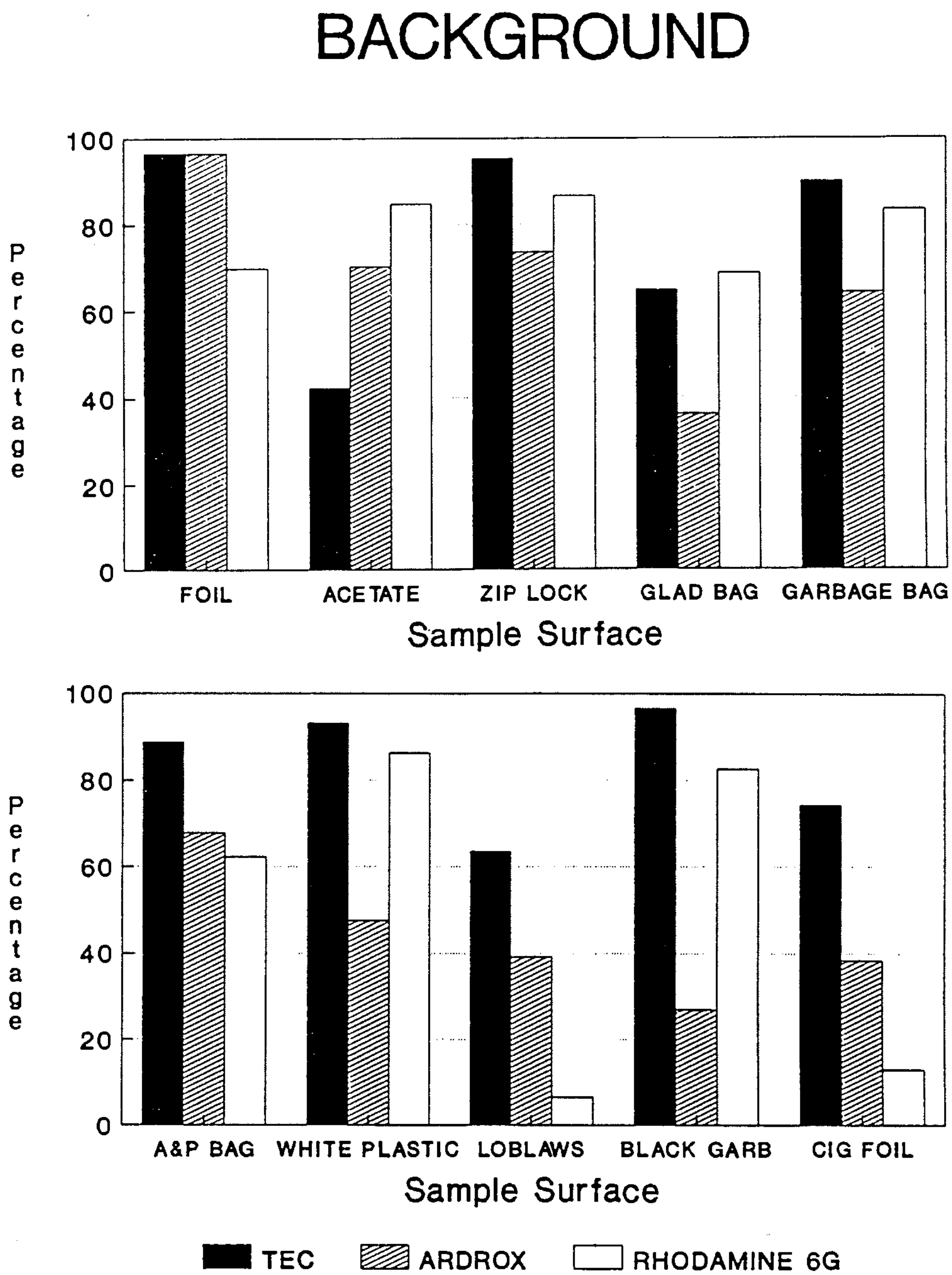

Figure 4 Percentage scores for background fluorescence for all ten surfaces. TEC (solid), Ardrox (hatched) and Rhodamine 6G (blank).

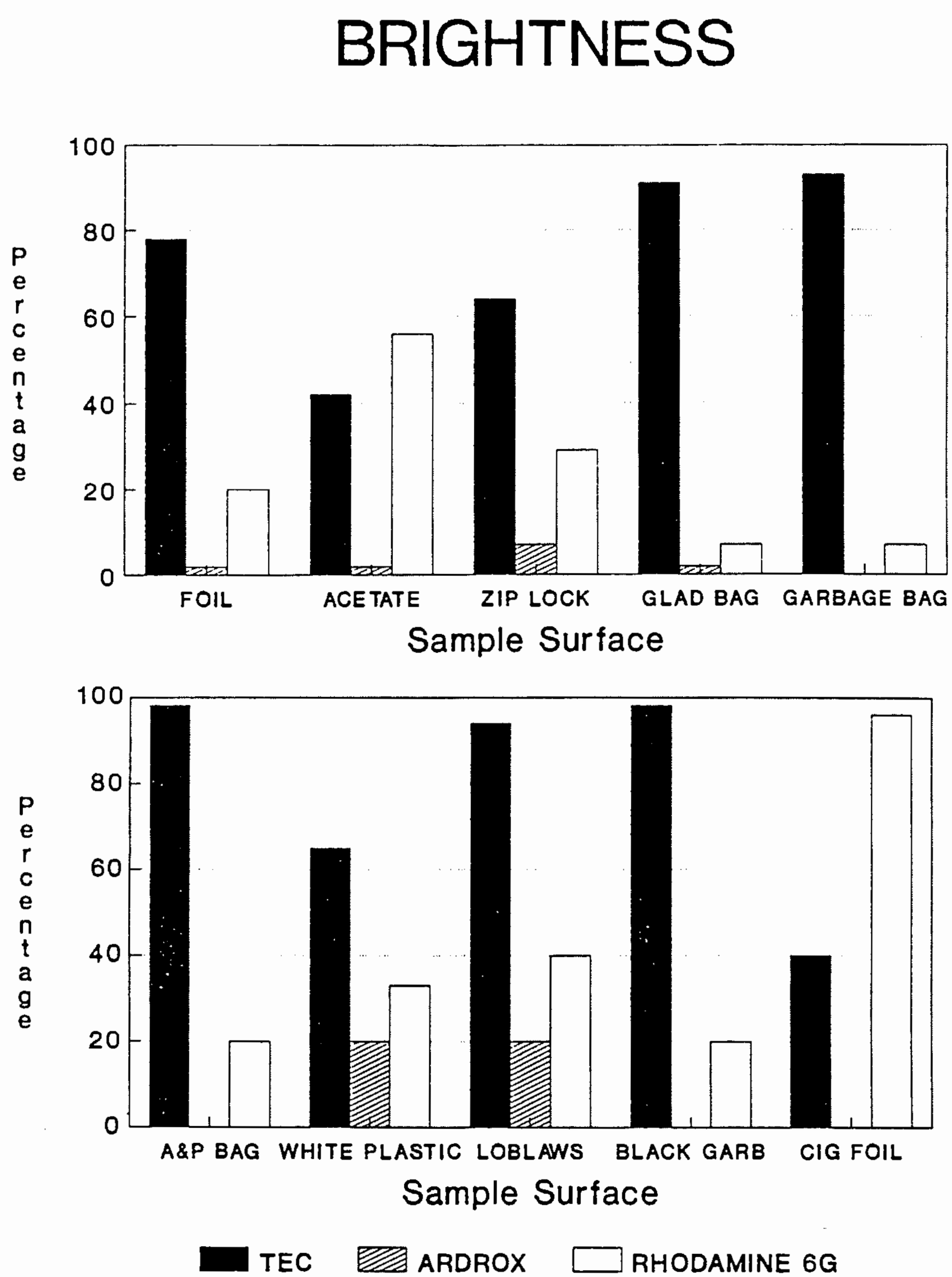

Figure 5 Percentage scores for print brightness for all ten surfaces. TEC (solid), Ardrox (hatched) and Rhodamine 6G (blank).

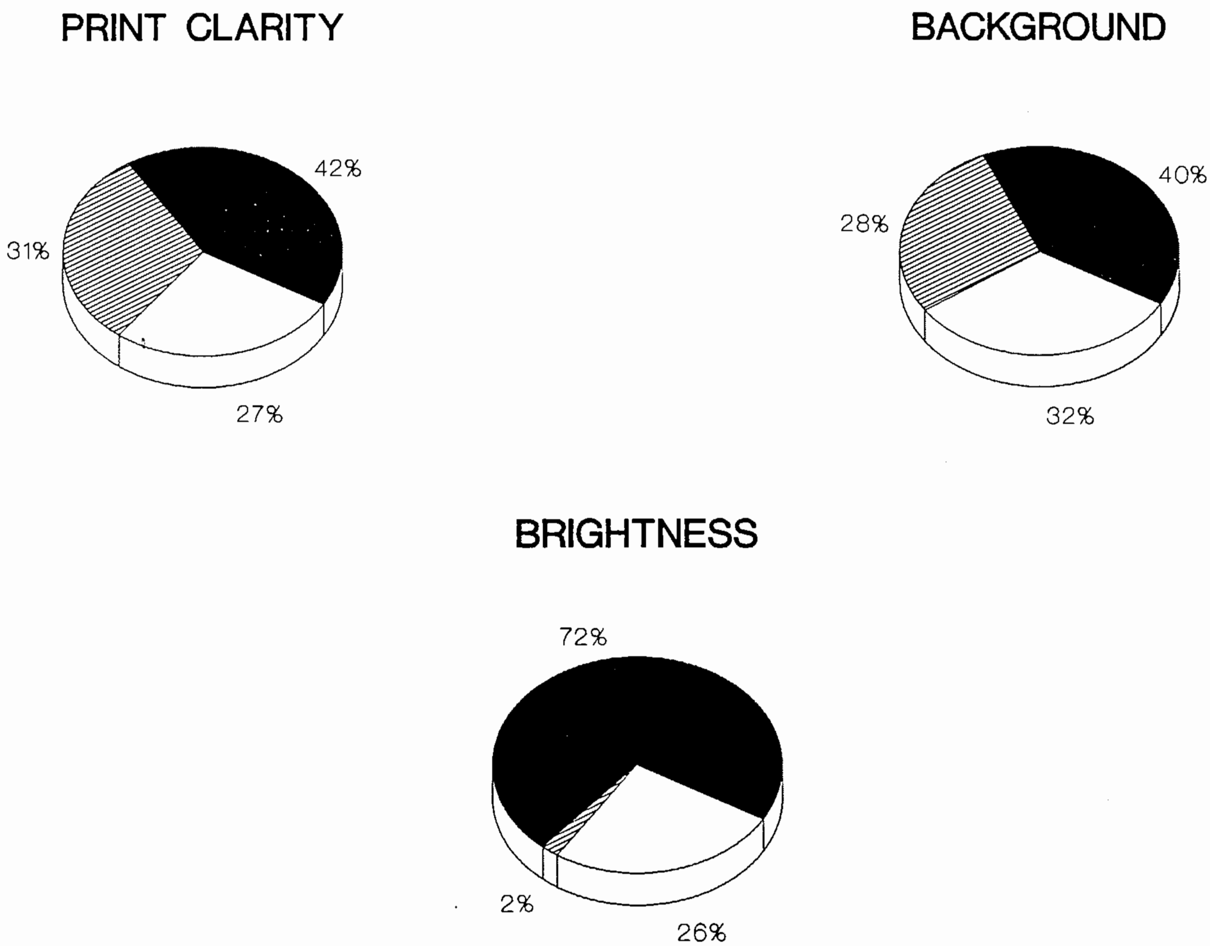

Figure 6 Percentage scores for (a) Print Clarity, (b) Background, and (c) Print Brightness for all samples combined. TEC (solid), Ardrox (hatched) and Rhodamine 6G (blank).