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Author(s): Brenda M. Bernier
Topics in Photographic Preservation, Volume 7.
Pages: 10-18
Compiler: Robin E. Siegel

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A Study of Poly (vinyl chloride) Erasers Used in the Surface Cleaning of Photographs

Brenda M. Bernier

I. Abstract:

Erasers are occasionally used to surface clean photographs of dirt and grime. Although the chemical composition and aging characteristics of erasers have been studied, published reports on the residual effects have dealt with cellulose materials and not photographic materials. This study is designed to investigate the composition of poly (vinyl chloride) erasers, as well as to evaluate their abrasive and residual effects on albumen and gelatin silver photographs.

II. Introduction:

The surfaces of photographs, particularly those with a gelatin binder layer, can be quite reactive with water. For this reason, photograph conservators have attempted to develop non-aqueous and dry cleaning methods while relying on techniques developed by paper conservators. While the proper and controlled use of erasers on paper can be a safe and effective technique, the effects of the same materials and techniques on photographs cannot be assumed. The additional components of a binder layer and a final image material result in different responses to abrasion, amount of eraser residue and the possible long term effects of such residue.

The composition of erasers used in conservation has been studied for a number of years including a 1966 study by the McCrone Associates investigating seventeen book cleaning materials[1] and in 1981 by the Canadian Conservation Institute[2] (CCI). Other studies have shown either the abrasive quality of erasers or the tendency of small eraser crumbs to become trapped within the interstices of the paper fibers.[3-5] Based on these and other studies, conservators frequently choose erasers made of poly (vinyl chloride)(PVC), such as Magic Rub® by Faber Castell and Mars Plastic® by Staedtler, in the belief that the aging properties of PVC are better than those of rubber or vulcanized vegetable oil found in other erasers.

Analytical testing conducted by CCI in 1981 has indicated that both Magic Rub® and Mars Plastic 52652® contain a dialkyl phthalate plasticizer, calcium carbonate, and a trace amount of titanium in addition to the PVC. The Magic Rub® also contained a trace amount of silicon. Of the six types of PVC erasers tested, Magic Rub® and Mars Plastic® contained the least amount of inorganic additives. Although the deterioration of PVC produces hydrogen chloride,[6] which can cause the oxidization of the silver image material of photographs, it was proposed by CCI that the erasers contained enough calcium carbonate to neutralize some of the acid. The presence of about 35% dioctyl phthalate plasticizer in the Magic Rub® eraser was confirmed by Faber Castell in the 1982 study by Pearlstein, etal.

Brenda M. Bernier is a Graduate Fellow in the Winterthur/University of Delaware Program in Art Conservation.

Since proprietary products are subject to change without notice from the manufacturer, this study was designed to investigate the compositions of Magic Rub® and Mars Plastic 52650® erasers, using x-ray fluorescence spectrometry for inorganic elemental analysis, and Fourier transform infrared spectrometry for the identification of organic compounds.

Additionally, the evaluation of abrasion, density loss and amount of eraser residue on treated photographs comprised the second part of this study.

A glossmeter was chosen to detect abrasion on the surfaces of the photographs. This device specifically measures the difference between the amount of incident light projected onto a surface and the amount of light reflected from that surface.[7] When a photograph is abraded more light is scattered from the resulting irregularities in the surface, therefore the amount of gloss decreases, as indicated by a lower numerical reading.

The densitometer measures the amount of opacity in an area, therefore it can be used to measure density changes of the silver image in a small area. This instrument is commonly used in the field of photograph conservation and was therefore an appropriate choice for this particular application.

As previously mentioned, the amount of eraser residue on cellulose materials has been studied, but there are no known published reports of eraser residue on photographs. The protein binder on albumen and gelatin silver prints is smoother than the surface of paper alone; however binders are often cracked, so it was unknown whether there would be more or less residue than would be found embedded in paper fibers alone. The use of before and after treatment photomicrographs was chosen in order to visually identify eraser particle residue.

If eraser particles do remain on the surface of the photograph, the long term effects of the residue upon aging are unknown. The Photographic Activity Test is a well used procedure designed to determine if a material in close contact with a photograph will cause fading or staining of the photograph over time.

Three smaller tests were included to investigate the plasticizers in the erasers. The first test was designed to determine the current relative amount of plasticizer in both eraser types. The other pilot studies were intended to determine if plasticizer could be detected on the surface of a treated photograph. These tests included both examining partially treated photographs with infrared reflectography, and attempting to extract the plasticizer from the surface of a treated photograph for FTIR analysis.

III. Procedures:

Eraser Characterization

The first method of eraser characterization was to simply visually analyze the two eraser types for differences. One sample each of the Magic Rub® and Mars Plastic® eraser was microscopically examined under both transmitted and incident light. The microscope used was a Nikon stereomicroscope with an E plan 10/.25 160 lens and a 10x objective, located at Winterthur Museum.

Three randomly selected samples of both the Magic Rub® and Mars Plastic® erasers were analyzed using Fourier transform infrared spectroscopy at Winterthur

Museum. Thin sections were taken and placed on a diamond cell and viewed on the XAD microscope attachment of a Laser Precision-Analect RFX-65 FTIR Spectrometer with a cryogenically cooled mercury cadmium telluride detector. At a resolution of 4 cm^{-1}, each sample was scanned three hundred times in order to reduce instrumentation noise. In a second set of samples, the organic components of the erasers were extracted with chloroform, forming a film when dried which was then analyzed as previously mentioned. Printouts were made of both types of analysis and through a computer search, the organic compounds were compared to references and identified.

Inorganic components were identified using a Kevex model 0750 X-Ray Fluorescence Analyzer, also located at Winterthur Museum. The same erasers used in the FTIR analysis were also used for this analysis. Areas of approximately 1 mm square were scanned for 150 seconds at a setting of 45 kilovolts and 0.4 milliamperes with a carbon target, in order to detect the presence of elements primarily with atomic numbers greater than 19. Printouts of the analysis were made and the major peaks identified.

Daniel M. Burge, Assistant Scientist at the Image Permanence Institute, Rochester Institute of Technology, performed the Photographic Activity Test on one sample each of the Magic Rub® and Mars Plastic® erasers. Without brushing, he pulled the eraser three times along a strip of Whatman No. 1 filter paper which was then used in the test package.[8] The test was conducted as per ANSI IT9.16-1993.[9]

Sample Preparation

Ten samples each of naturally aged albumen and gelatin silver developed-out prints (DOP) were supplied by Debra Hess Norris, Associate Professor at the University of Delaware. These were examined and categorized in terms of surface qualities such as gloss and cracking. Three templates were made from 3 mil polyester for each photograph. The first template covered the entire photograph but had two rectangular openings, measuring approximately 2 cm by 5 cm. The openings indicated where the eraser treatments were to occur and were appropriately numbered. The numbering system for the treatment areas included a three part number in which the first number identified the sample photograph from one to twenty. The second number indicated the type of photograph, with number 1 representing albumen and number 2 representing gelatin silver DOP. The final number designated which type of eraser was to be used for the study, such as number 1 for Mars Plastic® and number 2 for Magic Rub®. For example, a completely numbered sample may have been identified as 8-1-1. The numbering system aided in randomization during testing and statistical analysis afterwards.

The other two polyester templates fit over the rectangular openings and contained three holes at areas of low, medium, and high density which were identified as A, B, and C, respectively. These templates were used both in order to isolate areas of the sample to be measured with the densitometer and to be photographed under magnification.

Treatment Protocol

One sample area from each photograph was treated with the Magic Rub® eraser, while another was treated with the Mars Plastic®. The treatment of the photographs was an alteration of the previously mentioned study of Pearlstein, Cabelli, King, and Indictor. Instead of strips of sample photographs to be erased, the uncut photographs were erased

through the rectangular openings of the mylar templates. The erasers were angled so that one edge was in contact with the width of the opening then pulled with equal pressure five times along the length of the opening, then five times along the width. A clean hake brush was used to brush away the visible eraser crumbs. The order of the samples to be treated were randomly selected by drawing a treatment area number from an envelope.

In order to ensure that the composition of the erasers used were representative of Magic Rub® and Mars Plastic®, five erasers of each type were obtained, consisting of both new and old, but unused, samples. These were randomly selected so that each photograph was treated with one of the five Magic Rub® erasers as well as one of the five Mars Plastic® erasers.

Density and Gloss Measurements

Before treatment density measurements were taken using the reflectance head of a Macbeth TR924 Densitometer which had been calibrated to a standard. This instrument was located in the Photograph Conservation Laboratory of the University of Delaware. Sample areas, such as 10-1-2, were randomly chosen as previously described, however readings were always taken in the order A-B-C. Three readings were taken for each opening in the template and were averaged for a single density measurement of that area. Numbers were rounded to two decimal places. This process resulted in six density measurements for each photograph, or more specifically: a low, medium and high density area within each of the two areas that were to be treated with the erasers. The same procedure was used for the after treatment density measurements.

At the National Archives facility in College Park, Maryland, the before and after treatment gloss measurements were taken with a Macbeth Statistical Novo-Gloss glossmeter with the incident light set at 60°. Since the exact area being measured by the equipment could not be determined, and therefore could not be relocated for the after treatment measurements, only the templates with the rectangular openings were used. Ten readings were taken within each rectangular opening and averaged together to arrive at one gloss measurement for each area, for a total of forty average measurements for the entire sample set. As with the density readings, the order of the sample areas to be measured was randomly selected.

Statistical analysis on both the gloss and the density measurements were performed using the Microsoft® Excel 7.0 spreadsheet computer program.

Photomicrographs

Using TMax 100 black and white film, photomicrographs were taken of the low, medium, and high density areas as marked on the templates as A, B, and C. This resulted in a total of 120 before treatment images. At Winterthur Museum, a Nikon stereomicroscope with a Nikon-35A camera attachment and a Nikon HFX-II control was used. The magnification included an E plan 10/.25 160 lens with a 10x objective. Each photograph was placed directly on the microscope stage and two incident lights from an Intralux 6000 light source were set at approximately 45° from the surface of the photograph. In order to aid in sample identification when the contact sheets were viewed, the samples were photographed in strict order of the sample numbers, starting with sample 1-1-1-A and ending with 20-2-2-C.

After treatment, the samples were examined with the same microscope configuration and polyester templates in order to determine the presence of eraser residue. Using the before treatment contact sheets as a reference, it was difficult to find the *exact* areas for comparison, therefore, only representative after treatment photographs were taken.

Additional Pilot Studies on the Eraser Plasticizers

A small pilot study was carried out in order to determine the approximate amount of plasticizer in each of the eraser types. Janice Carlson, Museum Scientist at Winterthur Museum, extracted the plasticizer from one small piece each of the two eraser types in a chloroform bath over a period of a few weeks, until it appeared that no plasticizer remained. She then compared the before and after weights of the eraser pieces to arrive at the percent weight of the plasticizer.

Three of the sample albumens and three gelatin silver photographs were observed using infrared reflectography, or the IR Vidicon system equipped with a C2741 Hamamatsu video camera and a 634 Tektronix monitor. The templates were not used in order to determine if the treated areas reflected infrared light differently from the rest of the photograph, possibly due to the presence of residual plasticizer.

A second method of determining the presence of residual plasticizer was attempted. Two additional sample albumen photographs were procured so that one was left as a control while the other was completely surface cleaned with a Mars Plastic® eraser. Each surface was individually flooded with chloroform in order to extract any possible plasticizer. The chloroform was immediately recollected and allowed to evaporate in a fume hood so that the plasticizer extraction could become more concentrated in the watch glass and collected for FTIR analysis.

IV. Results:

Eraser Characterization

Using simple visual analysis, the Magic Rub® eraser was grayer, softer and had more voids which were particularly visible in the side view of the eraser. The Mars Plastic® was whiter and, as was seen under magnification, was made up of more regular agglomerates.

The thin sections of the two eraser types yielded similar spectra using the Fourier transform infrared spectrometer. Carbonate and carbonyl bands were visible. More informative, however, was the analysis of the plasticizer extracted with chloroform. Through a computer search, the two plasticizers were identified as a di-n-octyl phthalate for the Magic Rub® and a di-iso-decyl phthalate for the Mars Plastic®.

On both eraser types, x-ray fluorescence was used to detect the presence of chlorine and calcium. Other trace elements in the Magic Rub® eraser included strontium and iron, while the Mars Plastic® contained titanium.

Daniel M. Burge of the Image Permanence Institute evaluated the results of the Photographic Activity Test. He reported that both the Magic Rub® and the Mars Plastic® erasers passed all three criteria of the test: silver image interaction, gelatin staining, and mottling of image interaction detector.

Effects of Eraser Treatment on Sample Photographs

The percent change in gloss for the albumen photographs ranged from -14.94% to +54.43% so most statistical analysis was inconclusive. However, there appeared to be no difference between the two types of erasers and in general there seemed to be an increase in gloss because only five of the twenty test areas showed a negative percent change.

The percent change in gloss for the gelatin silver prints were wildly variable and no clear patterns emerged from the data. For example, in one photograph there was a decrease in gloss using the Magic Rub® and an increase in gloss using the Mars Plastic®. However, in another similar sample, the opposite results occurred. In general there may have been a slight decrease in gloss after treatment, however the standard deviation for this data is quite high.

For both the albumens and the gelatin silver prints there was an overall density loss of a few hundredths of a unit, or less than 5% loss. However, in the low density areas of the gelatin silver photographs, the same losses of a few hundredths of a unit resulted in an average percent change as high as -16%. Again there were no differences between the two eraser types.

The before and after photomicrographs were intended to allow a visual identification of abrasion or eraser particle residue. Even with the use of templates, the exact same area after treatment could only be found in two cases. This made identification of new scratches inconclusive. The evaluation of eraser particle residue was even less successful. Dust on the sample photographs and dustspecks on the photomicrographs both resembled the eraser particles. More important however, was the fact that the eraser particles tended to cling to the polyester templates due to static charge, therefore the amount of particulates remaining from the treatment itself could not be determined.

In order to better understand if this part of the study could be useful in the future, a few, very controlled before and after treatment photomicrographs were taken in different sample areas without the use of any template whatsoever. The surfaces of the gelatin silver samples were fairly featureless and yielded a few eraser particles. The albumens had a more varied topography so more eraser particles tended to remain, especially in the cracks. It was also noted that no abrasion was visible and the cracks did not appear to be any larger.

Additional Pilot Studies on the Eraser Plasticizers

Comparison of before and after weights of the eraser pieces that had the plasticizer extracted, indicated that the Magic Rub® was approximately 34.1% plasticizer by weight, while the Mars Plastic® eraser was about 55.2%.

Visual analysis with infrared reflectography showed no difference in reflection of the treated areas in any of the gelatin silver prints. Two of the three albumens did reflect infrared light differently in the areas treated with the Mars Plastic® eraser only.

The chloroform extraction of possible plasticizer on the treated sample yielded no residue that could be analyzed with FTIR.

V. Discussion:

Through Fourier transform infrared spectroscopy and the small study of percent weight of plasticizer, it was shown that the current plasticizer compositions of the two

types of PVC erasers are only slightly different from erasers of fifteen years ago. The Magic Rub® still contains approximately 35% di-n-octyl phthalate. The Mars Plastic® has been specifically determined to contain about 55% di-iso-decyl phthalate. The percent weight of plasticizer should be regarded with caution, however, since this was a pilot study and only one sample from each type of eraser was tested.

X-ray fluorescence revealed that both erasers contain chlorine from the PVC and calcium from calcium carbonate. One disadvantage to XRF is the fact that elements below atomic number 19 are generally not detected, therefore silicon was not detected although it was cited by CCI as being a trace element in the Magic Rub® eraser. However, even though chlorine is below atomic number 19, it was detected because it exists in such a great amount. Chlorine could be problematic because hydrochloric acid could be formed upon aging if any residue is left on the surface of the photograph. However CCI believes that there is enough calcium carbonate present to neutralize this threat. Other trace elements in the Magic Rub® include strontium and iron, which could also be a problem. The Mars Plastic® contains titanium which accounts for its white color.

It must be stated that the treatment protocol called for an eraser cleaning method that was much more aggressive than what would normally be used by a photograph conservator, however consistency of application was the main concern.

The glossmeter proved to be a sensitive enough instrument to detect small changes in gloss that were not visible to the human eye. The general increase in gloss on the treated albumen photographs may probably be due to the removal of an irregular dirt layer which had acted to scatter the light. Another possible explanation for the increase in gloss may be a deposition of a smooth plasticizer residue. The data on the gelatin silver prints could possibly be more clear if a larger sample set was used, or if the samples chosen were more similar in surface characteristics. For both the albumens and the gelatin silver prints, perhaps similar testing should be carried out on more uniform, newly fabricated sample photographs.

It is unknown if the overall loss of density was due to loss in silver image material or simply a dirt layer. As with the gloss measurements, this part of the study should be repeated with new, clean sample photographs. Since the density readings of the low density areas on the gelatin silver prints were very low, any small loss in density resulted in a particularly high percent change. Statistically separating the low density areas appeared to work well in preventing an artificial inflation of the overall density loss.

Taking the photomicrographs in strict order of the sample numbers was an effective method of identification. However, the photomicrographs were not successful because of the major problem of eraser residue clinging to the polyester templates due to static charge and the fact that the openings on the templates were too large. A possible alteration of this technique would be to first make the templates with smaller openings over the density areas, then to keep them away from the photographs during treatment. The treatment templates with the rectangular openings should be removed after treatment and the photographs brushed of residue. The clean templates with the small holes could then be replaced in order to take the after treatment photomicrographs.

Scanning electron microscopy (SEM) was not used in this study because it is a destructive technique, so the exact same locations for the before and after treatment

analysis could not be provided. However, SEM merits further investigation for detection of abrasion and eraser residue, particularly if more uniform sample photographs are used.

Evidence from the gloss measurements of the albumens *combined* with the sample photomicrographs indicate that aggressive eraser treatment caused no appreciable physical damage to the albumen photographs in the form of abrasion or increased cracks. The evidence for abrasion of the gelatin silver photographs, however, was inconclusive.

In the sample photomicrographs, particulate residue was visible, particularly on the albumens. As previously stated, the inorganic components and plasticizer in the residue could cause deterioration of the silver image over time. Since the research stated in the introduction considered only the thermal degradation of PVC, perhaps a study of the effects of light aging of PVC would more closely simulate the actual aging of eraser residue on photographs. In either case, the results from the Photographic Activity Test indicated that the residue may not be a significant threat. However, only one sample from each type of eraser was evaluated so these results should be considered preliminary. If the PAT is repeated on the erasers, perhaps a larger sample set could be used or even the amount of eraser residue on the Whatman filter paper could be increased.

Finally, more research needs to be done to determine the extent of plasticizer remaining on the surface of the photographs. Infrared reflectography may have potential for this application. Two of the six photographs examined showed some reflectance in the areas treated with the Mars Plastic® eraser, which was the eraser type with the higher percent of plasticizer. However, the results were subtle and could easily be misinterpreted so further study of this technique is advised. The extraction of the plasticizer on the treated photograph was unsuccessful, even though the sample had been heavily eraser cleaned. But again, this was only a pilot study so the use of a larger sample set may yield results.

This study demonstrated that there is no significant difference between the Magic Rub® and the Mars Plastic 52650® erasers in terms of gloss or density changes. A decision to use either of the erasers for surface cleaning of photographs should instead be based on the composition of the eraser and its working properties.

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VII. Acknowledgments:

I would sincerely like to thank the following for their invaluable contributions to this research: Janice Carlson, Museum Scientist at Winterthur Museum who performed all

solvent work and both the XRF and FTIR analyses, as well as provided crucial guidance throughout the research; Richard C. Wolbers, Associate Professor at the University of Delaware who was the Research Advisor for this study and offered advice and instruction in photomicroscopy; Daniel Burge and the Image Permanence Institute who generously performed the Photographic Activity Test; Debra Hess Norris, Associate Professor at the University of Delaware who initially suggested the need for this research and supplied sample photographs; Sarah Wagner at the National Archives, College Park, Maryland who offered the use of the glossmeter and Steven Puglia who provided instruction; and Herbert Crosson, Museum Photographer at Winterthur Museum who assisted with the infrared reflectography.

May, 1996