RESUMO

As placas autochrome foram o primeiro processo fotográfico a côr comercialmente viável. A fraca estabilidade à luz dos corantes presentes no ecrã de côr levaram a maioria das instituições culturais com este tipo de material a adoptarem uma política de não exibição de originais, recorrendo ao uso de fac-similes. A presente investigação, levada a cabo no Metropolitan Museum of Art em Nova Iorque, estudou a estabilidade à luz, sob uma atmosfera de baixo oxigénio, dos seis corantes presentes no ecrã de côr das placas autochrome – Tartrazina, Eritrosina B, Rosa Bengala, Azul Patente, Cristal Violeta, e Azul Flexo.

Os corantes foram testados individualmente na primeira fase da investigação e, na segunda fase, nas combinações vermelho-laranja, verde e azul-violeta presentes no ecrã de côr das placas autochrome. Amostras produzidas seguindo as formulações históricas foram expostas a 8.29 horas megalux. Foram recolhidas leituras espectrofotométricas antes e após a exposição à luz. Um grupo de amostras foi exposto numa atmosfera de baixo oxigénio (menos de 0.1%) e um segundo grupo comparativo foi exposto à luz em condições atmosféricas de oxigénio (cerca de 21%). Os resultados indicam o benefício das condições de baixo oxigénio em retardar o grau de desvanecimento do ecrã de côr das placas autochrome expostos a elevados níveis de luz.

Os resultados desta investigação permitiram o *Metropolitan Museum of Art* exibir placas autochrome originais pela primeira vez em mais de vinte-cinco anos, no âmbito da exposição *Stieglitz, Steichen, Strand*. Cinco placas autochrome da autoria de Alfred Stieglitz e Edward Steichen foram expostas em atmosfera de baixo oxigénio durante uma semana em Janeiro de 2011. Durante o restante período da exposição foram utilizados fac-similes. A terceira fase desta investigação consistiu no desenho, teste e implementação de uma embalagem selada de baixo oxigénio; na investigação de fontes de luz para exposição; no estabelecimento da metodologia de monitorização antes, durante e depois da exposição; e no desenho do método de exibição dos fac-similes.

Palavras-chave: placa autochrome; atmosfera de oxigénio reduzido; desvanecimento à luz; corantes; exposição; embalagem selada

ABSTRACT

The autochrome was the first commercially viable photographic color process. The poor light-fastness of the dyes present in the autochrome's color screen caused the majority of cultural institutions to have a policy of not displaying original plates but facsimiles instead. This research, carried out at The Metropolitan Museum of Art in New York between 2007 and 2010, focused on the light-fastness, under low oxygen conditions, of the six dyes present in the autochrome color screen – Tartrazine, Erythrosine B, Rose Bengal, Patent Blue, Crystal Violet, and Flexo Blue.

In a first stage of research the dyes were tested individually and in a second stage they were tested in the red-orange, green and blue-violet combinations as found in the autochrome color screen. Samples produced following the historic formulations were exposed to 8.29 Megalux·hours of light. Spectrophotometric data was collected before and after exposure. For one sample group, a closed setup was designed that created a low-oxygen environment (less than 0.1 percent). A comparison group was exposed to light in normal air conditions (about 21 percent of oxygen). Results indicate a benefit of near anoxia in slowing the fading rate of the autochrome color screen at high levels of light exposure.

The results of this research allowed The Metropolitan Museum of Art to exhibit original autochrome plates for the first time in over twenty-five years as part of an exhibition entitled *Stieglitz, Steichen, Strand*. Five autochromes by Alfred Stieglitz and Edward Steichen were displayed in nearly anoxic conditions for one week in January 2011. Facsimiles were displayed for the remainder of the exhibition.

The third stage of this research consisted of the design, test and implementation of a low-oxygen sealed package; the investigation of light sources used for display; the establishment of monitoring methodology before, during and after exhibition; and design of the method for facsimile display.

Keywords: autochrome; low-oxygen; light-fading; dyes; exhibition; sealed package

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Índice

1. Introdução

As placas autochrome são objectos fotográficos complexos. Tratam-se de transparências de imagem positiva num suporte de vidro que têm que ser vistas sobre uma fonte de luz. Tal como no caso do daguerreotipo, a placa autochrome é um objecto único, um positivo directo, em que não existe uma matriz com possibilidade de fazer múltiplas cópias.

Figura 1: Placa sutochrome sob iluminação reflectida (acima) e iluminação transmitida (abaixo). "Clarence White", por Edward Steichen, 1907. MMA 55.635.19

As suas necessidades de preservação específicas foram caracterizadas no passado em diversos estudos aprofundados e compreensivos. As preocupações de preservação com estes objectos incluem a fragilidade física do suporte em vidro e a sensibilidade dos vários componentes à temperatura, humidade relativa e luz. Esta última é particularmente detrimental aos corantes do ecrã de côr. A fraca estabilidade à luz destes corantes levou a que a maioria das instituições culturais na posse de placas autochrome estabelecessem uma política de não exposição destes originais.

Estudos de anóxia aplicada a materiais presentes em bens culturais demonstram que os mecanismos de desvanecimento de certos corantes ocorrem devido a foto-oxidação e que quando expostos à luz em condições de baixo ou nulo valor de oxigénio esta forma de deterioração não ocorre.

A investigação que propus realizar enquanto *Research Scholar in Photograph Conservation* no Metropolitan Museum of Art, entre Setembro de 2007 e Setembro de 2010 teve por objectivo determinar os efeitos de ambientes anóxios nos corantes presentes nas placas autochrome quando

exposto à luz, com vista a uma solução que permitisse a exibição destes originais de grande interesse cultural e estético.

No decurso da investigação, uma vez que o protocolo experimental usado recorreu a indicadores de oxigénio de que detectam estes gás a valores mínimos de 0.1%, tornou-se evidente que seria incorrecto a referência a anóxia mas que o termo correcto dos resultados seria o de um estudo de ambientes em baixo oxigénio.

Outra componente do projecto foi a definição do protocolo de aplicação dos resultados através do desenho e teste de uma embalagem selada de baixo oxigénio; investigação de fontes de luz para exposição; e estabelecimento da metodologia de monitorização antes, durante e depois da exposição.

Os vários aspectos desta investigação foram apresentados publicamente nos seguintes colóquios:

- "Research on Low-Oxygen Environments Applied to Autchrome Plates at The Metropolitan Museum of Art", com Masahiko Tsukada e Nora Kennedy. 21 de Outubro de 2011, WAAC Annual Meeting and Conference. Austin TX, EUA.
- "Light-fastness of Autochrome Color Screen Filters Under Anoxic Conditions", com
- Masahiko Tsukada e Nora Kennedy. 19 de Setembro de 2011, ICOM-CC 16th Triennial Meeting. Lisboa, Portugal.
- "Display of Original Autochrome Plates in Low-Oxygen Enclosures at The Metropolitan
- Museum of Art", com Nora Kennedy, Katherine Sanderson e Masahiko Tsukada.
- 12 de Setembro de 2011, Anoxia and Microfading: The Impact on Collection Care Conference. Tate Modern, Londres, Reino Unido.
- "Display of Alfred Stieglitz and Edward Steichen Autochrome Plates: Anoxic Sealed
- Package and Lighting Conditions", com Katherine Sanderson. Fevereiro de 2011, PMG Winter Meeting. Ottawa, Canada.
- "Light Fading of Autochrome Dyes Under Anoxic Conditions". 19 de Outubro de 2010, ICOM-CC Photographic Materials Interim Meeting. Benaki Museum, Atenas, Grécia.

- "Autochromes on View: Effects of Anoxia on Dye Stability", 27 de Abril de 2010, Fellows Colloquia. The Metropolitan Museum of Art, New York, NY, EUA
- "Light Fading of Autochrome Screen Dyes Under Anoxic Conditions". 14 de Maio de 2010, AIC 38th Annual Meeting. Milwaukee, WI, EUA.
- "Anoxic Environments Applied to Autochrome Plates". 12 de Maio de 2009, Fellows Colloquia. The Metropolitan Museum of Art, New York, NY, EUA
- "Research on Autochrome Preservation". 24 de Janeiro de 2009, PMG Winter Meeting. Tucson AZ, EUA
- "Color-Mad: Preliminary Research in Autochrome Preservation". 13 de Maio de 2008, Fellows Colloquia. The Metropolitan Museum of Art, New York, NY, EUA

Esta investigação foi também publicada nos seguintes jornais e actas:

- "Effects of Low Oxygen Environments in the Light Fading of Six Dyes Present in the Autochrome Color Screen" (2012). Coautor Masahiko Tsukada. *Journal of the American Institute for Conservation*, Fall/ Winter 2012, Vol.51, Number 2. AIC, Washington D.C. pp. 159-174.
- "Display of Alfred Stieglitz and Edward Steichen Autochrome Plates: Anoxic Sealed Package and Lighting Conditions" (2011). Coautora Katherine Sanderson. *Topics in Photographic Preservation,* Vol. 14. AIC, Washington D.C. pp. 162-167.
- "Behavior of Autochrome Color Screen Dyes Under Anoxic Conditions" (2011). *Topics in Photographic Preservation,* Vol. 14. AIC, Washington D.C. pp. 52-58.
- "Light-fastness of autochrome color screen filters under anoxic conditions" (2011). Coautoria Masahiko Tsukada e Nora Kennedy. *ICOM-CC 16th Triennial Meeting Preprints*. pp. 1-9.
- "Autochrome Research at The Metropolitan Museum of Art: Testing Methodology and Preliminary Results for Anoxia Light-Fading" (2009). *Topics in Photographic Preservation*, Vol. 13. AIC, Washington D.C. pp. 128-136

O trabalho desenvolvido no Metropolitan Museum of Art teve por supervisora Nora Kennedy, chefe da área de Conservação de Fotografia, e o apoio técnico-científico do Departamento de Investigação Científica, em particular de Masahiko Tsukada. A aplicação final da investigação, que permitiu a exibição pela primeira vez em mais de vinte-cinco

anos de placas autochrome originais no Metropolitan Museum of Art, teve a colaboração da conservadora de fotografia Katherine Sanderson. As apresentações públicas da investigação e artigos publicados tiveram a colaboração e coautoria dos três.

A presente tese apresenta as publicações resultantes dos vários momentos da investigação como capítulos 3, 4 e 5. O capítulo 2 é uma introdução histórica e técnica do processo fotográfico e da colecção de autochromes do Metropolitan Museum of Art que foi o caso-estudo deste projecto.

2. As placas autochrome

2.1. Introdução histórica

As placas autochrome foram o primeiro processo fotográfico em côr comercialmente viável. Patenteado pelos irmãos Louis e Auguste Lumière[1] em França em 1903 e nos Estados Unidos da América em 1906, o processo começou a ser comercializado em 1907. As placas foram produzidas até 1935 quando o processo de côr cromogénia as veio substituir. Um processo posterior aos autochrome de transparências a côr em suporte de nitrato de celulose denominado *Filmcolor* foi comercializado pela casa Lumière até à década de 1950, de estrutura e materiais idênticos ao processo autochrome mas utilizando corantes diversos.

As placas autochrome são um processo de ecrã de côr aditivo. Este termo deriva do uso de um sistema de filtros de côr que permite criar uma imagem final a côres. O sistema de côr aditivo funciona pelo adição das côres vermelho, verde e azul para obter uma imagem (no caso das placas autochrome pela justaposição de filtros nestas côres). Na práctica este sistema funciona por projecção e foi utilizado pelos primeiros processos fotográficos em côr. Em contraste, o sistema subractivo baseia-se na sobreposição das côres cião, magenta e amarelo, e é usado em fotografia impressa de imagens a côr.

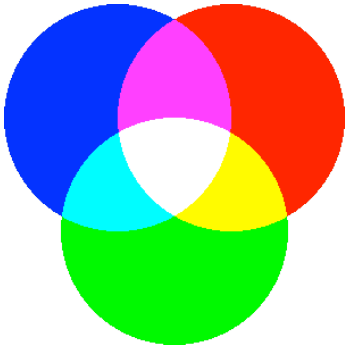

Figura 2: Diagrama do sistema de côr aditivo

A base para os processos fotográficos de côr aditivos foi demonstrada em 1861 por James Clerk Maxwell (Newhall 1982, p.272). Maxwell produziu três transparências positivas, representando uma fita em xadêz vermelho, verde e azul, que foram fotografadas através de três filtros distintos (vermelho, verde e azul); as transparências foram subsequentemente

[1] Embora Louis Lumière tenha inventado o processo, as patentes incluem os nomes de ambos irmãos. Anteriormente, em 1895, os Lumière haviam desenvolvido um processo experimental de montagem tricolor em vidro denominado *Chroma* que patentearam em França em 1903.

sobrepostas por projecção, recorrendo a três projetores separados com luzes das côres correspondentes a cada transparência, formando uma única imagem a côr[2].

O uso de um ecrã de côr para obter uma imagem fotográfica a côres foi descrito por Louis Ducos Du Hauron em 1868 que recorreu a um ecrã de côr composto de finas linhas côr transparentes. Outros dois processos fotográficos de ecrã de côr foram introduzidos antes das placas autochrome por John Joly em 1894 e James McDonough em 1896 sem grande sucesso comercial ou práctico.

As primeiras emulsões fotográficas tinham sensibilidade apenas às regiões azul, violeta e ultravioleta do espectro de luz. Em 1873 o cientista alemão Hermann Vogel descobriu a sensibilização espectral pela adição de corantes às emulsões. Demorou até 1906 a que uma emulsão totalmente pancromática (i.e. sensível a todas as côres visíveis do espectro de luz) fosse produzida com sucesso de forma consistente e comercializável (Coe 1978, p.34-39).

Embora o autochrome tenha sido o processo fotográfico a côres a ter maior sucesso comercial, diversos processos de ecrã de côr aditiva co-exitiram e foram comercializados nesta altura, tais como: Joly (1895), Warner-Powrie (1907), Omnicolore (1907), Paget (1913), Agfa Colour (1916), Finlay (1929), Dufaycolor film (1935), entre outros[3].

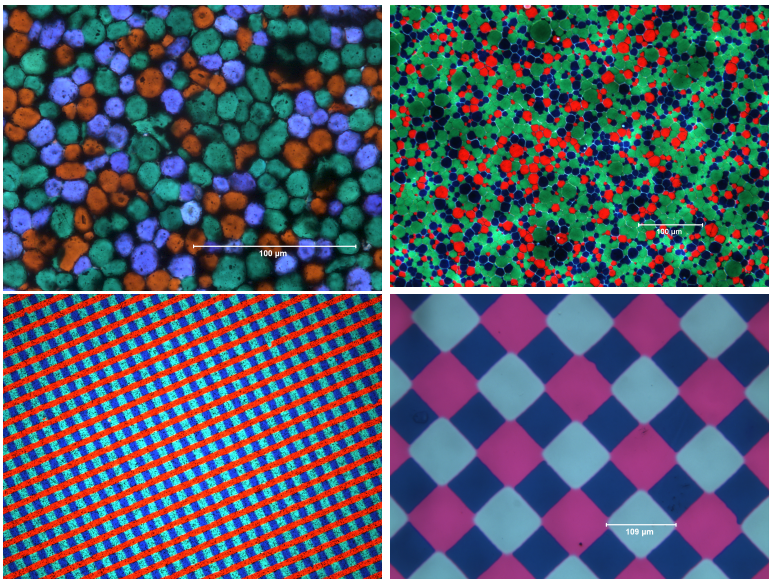

Figura 3: Exemplos de ecrãs de côr de processos fotográficos. De cima para baixo, da esquerda para a direita: Autochrome, Agfa Colour; Dufaycolor; placa. Fotomicrografias cedidas por Gawain Weaver

[2] Na realidade a emulsão fotográfica utilizada por Maxwell não tinha sensibilidade aos vermelhos do espectro de luz, mas captou, sim, a fluorescência emitida pelos corantes utilizados na altura para tingir a fita axadrezada (Newhall 1982, p.272).

[3] Brian Coe refere ainda Krayn line (1907), Krayn mosaic (1907), Thames (1908), Dufay Dioptichrome (1909), Aurora (1909), Leto (1913), Baker Duplex (1926), Lignose Film (1926). (Coe 1978, p.50-51).

2.1.1. O processo autochrome e os *Photo-Secessionists*

O movimento Pictorialista, também chamado *Photo-Secession* (Foto-Secessão), surgiu em cerca de 1900, e tinha como objectivo elevar a Fotografia ao estatuto de Bela-Arte. A estética associada com este movimento é marcada pelas imagens fotográficas encenadas, pela extensa manipulação dos processos fotográficos com preferência por técnicas como as gomas bicromatadas, pela manipulação da imagem através de retoque de negativos e impressões ou sobreposição de múltiplos negativos, e pelo uso de cartões de montagem elaborados. Alfred Stieglitz e Edward Steichen foram duas figuras proeminentes associadas com este grupo e tomariam um papel fundamental na importação do processo autochrome para os EUA. Ambos estavam em Paris quando o processo foi apresentado em 1907 pelos irmãos Lumière no *photo-club* daquela cidade, sendo que Steichen esteve presente na sessão (Passafiume 2005, p.315). Foi Alfred Stieglitz quem apresentou as placas autochrome pela primeira vez nos EUA numa conferência de imprensa na sua galeria *Little Galleries of the Photo-Secession* em Nova Iorque, a 27 de Setembro de 1907 (Nickel 1992, p.31). Na sua revista de arte fotográfica *Camerawork*, Stieglitz exulta o processo dos Lumière (Stieglitz 1907, p.20-25) e dedica em Abril de 1908 um número da publicação a imagens produzidas com placas autochrome. Vários fotógrafos pictorialistas começaram a practicar o processo com grande entusiasmo, possivelmente pela afinidade da imagem do autochrome com o pontilhismo na pintura francesa da época. E porém, perto de 1915 os membros deste grupo pararam de utilizar o processo, sem que exista registo do motivo específico para esta interrupção. Anne Hammond (History of Photography 1994, p.110) sugere como possíveis razões a reduzida margem de manipulação que o processo permitia, e o excessivo detalhe da imagem num resultado demasiadorealista.

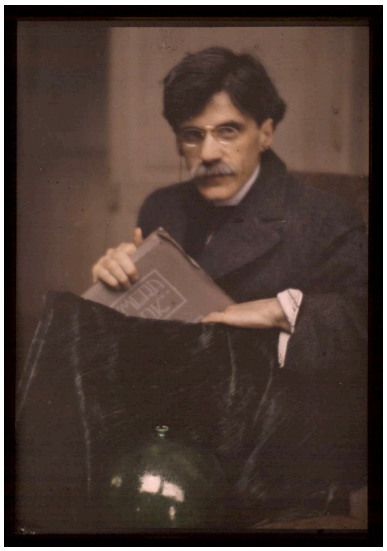

Figura 4: “Alfred Stieglitz”, por Edward Steichen, 1907. MMA 55.635.10

2.2. Descrição do processo e componentes físicas

2.2.1. Componentes materiais

A estrutura laminar da placa autochrome era composta do suporte em vidro onde se sobrepunham uma primeira camada de verniz dammar misturado com borracha natural que permanecia aderente por forma a conter a camada de grãos de fécula de batata tingidos de vermelho-laranja, verde e azul-violeta que compunham o ecrã de côr; os grãos eram pressionados numa prensa de forma a se tornarem achatados e mais transparentes; para cobrir os interstícios entre os grãos de fécula era aplicado pó de carvão; seguia-se uma segunda camada de verniz dammar; sobre esta era aplicada uma emulsão fotográfica de gelatina e prata pancromática que compunha a camada fotossensível (Lavédrine et.al.2005, p.134; Lavédrine et.al. 1993, p.142).

2.2.2. Exposição e Revelação

As placas autochrome eram produzidas exclusivamente pela empresa *Lumière et Ses Fils*, e vendidas prontas a expôr numa câmara fotográfica comum. O único ajustamento a realizar pelo fotógrafo era o uso de um filtro amarelo em frente da lente para evitar uma tonalidade azul na imagem, uma vez que ainda que pancromática a emulsão tinha uma maior sensibilidade à região de ondas curtas do espectro de luz (azuis e violetas).

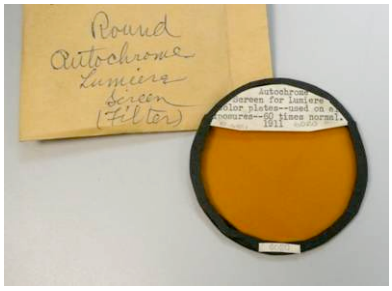

Figura 5: Filtro amarelo utilizado para fotografar autochomes. Colecção tecnológica da George Eastman House. *Imagem cedida por GEH/ Todd Gustavson*

A placa autochrome era colocada com o vidro na direcção do objecto a fotografar, de forma a que a luz fosse registada na emulsão filtrada através do ecrã de côr.

Durante a exposição, os grão coloridos do ecrã de côr funcionam como filtros. Ao fotografar, por exemplo, um objecto vermelho, a luz vermelha reflectida do objecto passa através dos grão de fécula tingidos de vermelho e afecta a emulsão.

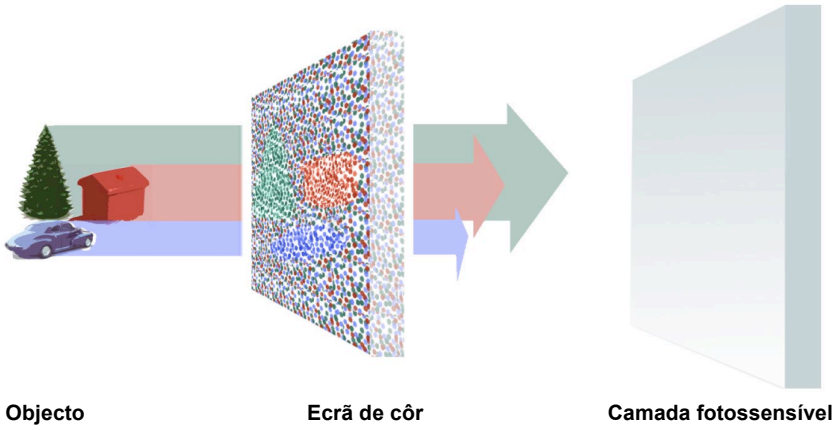

Figura 6: Diagrama de exposição da placa autochrome

O processo é uma imagem transparente positiva o que implica dois momentos de revelação (processo diapositivo).

Figura 7: Diagrama da revelação da placa autochrome

Depois da primeira revelação isto resulta numa área de prata reduzida opaca na emulsão fotossensível correspondente às zonas dos filtros vermelhos. A luz vermelha é absorvida pelos filtros azuis e verdes do ecrã de côr e, por isso, a emulsão fotossensível nessas zonas mantém-se inalterada (não exposta à luz).

Em seguida, a placa autochrome é colocada num banho de branqueamento que dissolve as zonas de prata exposta, anteriormente reduzida, mas não afecta as zonas não expostas. De seguida, a placa é exposta à luz ou enevoada quimicamente de forma a afectar as zonas remanentes (no nosso exemplo correspondendo às zonas dos grãos azuis e verdes) e revelada uma segunda vez, revertendo os tons da camada fotossensível – no nosso exemplo a área correspondente aos filtros vermelhos está agora transparente, e as áreas

correspondentes aos filtros azuis e verdes está agora opaca. Daqui resulta uma imagem transparente positiva na camada da emulsão.

Após a revelação, era comum a aplicação de uma camada de verniz, de resina natural ou celulósico, para proteger a imagem de humidade ou abrasão (Passafiume 2005). O verniz contribuía ainda para uma imagem mais saturada e transparente, aumentando a saturação das cores.

O último passo era a selagem da placa autochrome contra um vidro secundário do lado da emulsão com uma fita activada por calor ou humidade, sendo a primeira era recomendada pela empresa Lumière uma vez que a exposição a humidade facilmente arriscava a diluição dos corantes do ecrã de côr.

A visualização correcta de uma placa autochrome é feita do lado da emulsão. As placas eram visualizadas por luz transmitida, usando um *diascope* ou pendurando as placas numa janela, ou por luz projectada, recorrendo a uma lanterna mágica.

Figura: 8 Diascope da colecção tecnológica da George Eastman House. Imagem cedida por Todd Gustavson

Figura 9: A placa autochrome é colocada de cabeça para baixo no diascope, direccionada para uma fonte de luz, e visualizada no espelho na base do aparelho.

Figura 10: Exemplo de uma placa autochrome numa moldura de latão comercial intendida a ser pendurada de uma janela. Por esse motivo o vidro posterior é burilado de forma a difundir a luz. Esquerda: iliminação reflectida; direita: iluminação transmitida. Imagem cedida por Scott Bilotta.

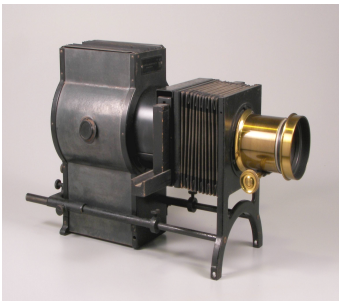

Figura 11: Lanterna mágica da colecção tecnológica da George Eastman House. Imagem cedida por Todd Gustavson

2.3. Aspectos de preservação e conservação

A fragilidade das placas autochrome é aparente no suporte de vidro que pode potencialmente ser quebrado ou deteriorar; e pelos componentes da imagem que podem desvanecer ou sofrer alterações de côr, ou delaminar do suporte ou entre si. O facto de que a imagem tenha que ser vista com recurso a uma fonte de luz implica a exposição a esta e a resultantes variações em temperatura e humidade relativa – todos agentes de deterioração dos componentes da placa autochrome (Krause 1985).

Figura 12: Exemplo de deterioração avançada do vidro de protecção

Formas de deteriorações frequentemente encontradas em placas autochrome são: vidro quebrado; deterioração do vidro (traduzida em enevoamento pontual, parcial ou total); formação de espelho de prata na imagem.

É também frequente encontrar os seguintes fenómenos: delaminação da camada da imagem (separação do suporte de vidro ou entre as várias sub-camadas); formação de pontos ou manchas verdes; alterações de côr do ecrã ou camadas de verniz. Estes efeitos podem ser formas de deterioração ocorridos ao longo do tempo como resultado de variações de temperatura e/ ou humidade relativa, exposição a gases nocivos (tais como gases de poluição ambiental, fumos, ou provenientes de mobiliário ou pintura de parede em salas de arquivo), ou exposição a água. Mas estes fenómenos podem também ser o resultado de problemas ocorridos durante o processamento da placa.

Medidas de conservação preventiva são essenciais para abrandar processos de deterioração.

As placas autochrome devem ser armazenadas dentro de embalagens de protecção compostas de materiais não-reactivos que tenham passado o teste de actividade fotográfica PAT. As placas em embalagens individuais devem ser colocadas dentro de uma caixa, também testada com o PAT, com material de acolchoamento na base para reduzir vibrações.

O ambiente na sala de depósito deve manter valores de humidade relativa baixos e estáveis – idealmente entre 35% e 45% com variações inferiores a 5% - e de temperatura inferiores a 18◦C. O congelamento de placas autochrome não é aconselhável pelo risco de

delaminação da camada da imagem em resultado de movimentos de expansão e contracção diferencial dos vários componentes.

2.4. Aspectos referentes à exibição e manuseamento

Os componentes mais vulneráveis das placas autochrome são, muito provavelmente, os corantes de tingimento dos filtros no ecrã de côr. Teste de desvanecimento à luz demonstraram a fraca permanência destes elementos (Lavédrine et.al. 1993, Lavédrine et.al. 2009) e as directrizes de conservação classificam estes objectos como "*extraordinarily light-sensitive*"[4] (Wagner et.al. 2001). Por consequência, a grande maioria de instituições culturais com autochromes nas suas colecções tem uma política de exibição de fac-similes, reduzindo ao mínimo a exposição de originais. Um inquérito informal realizado a conservadores de fotografia de instituições com importantes colecções de autochrome demonstrou que a maioria recomenda a não exibição de originais[5].

Figura 13: Autochrome originais em exibição no Amon Carter Museum. O interruptor de luz é activado pelo público. Imagem cedida por Sylvie Pénichon

Casos raros de exposição de originais recorreram ao uso de fontes de luz activadas pelo público, de forma a reduzir ao mínimo a exposição dos originais, como no caso da exposição "*100 Years of Autochrome*" no Amon Carter Museum em Fort Worth Texas (ver figura 13), dedicada ao processo.

O manuseamento das placas autochrome deve ser feito com extremo cuidado. O uso de luvas é desencorajado uma vez que reduz a sensibilidade das mãos. Preferencialmente, deve manusear-se as placas com mãos lavadas e secas, mantendo o objecto suportado sempre que possível. Durante observação, a placa deve ser mantida sobre uma superfície limpa. As placas não devem ser mantidas sob exposição a luz, incluindo a luz ambiente de

[4] Extraordinariamente sensíveis à luz

[5] Foram recolhidas respostas de: LeeAnn Daffner (Museum of Modern Art, New York); Jean-Paul Gandolfo (École nationale Louis Lumière, Paris) ; Toshiaki Koseki (Museum of Fine Arts, Houston); Connie McCabe (National Gallery of Art, Washington); John McElhone (National gallery of Art, Ottawa); Sylvie Pénichon (Amon Carter Museum, Fort Worth); Doug Severson (Art Institute of Chicago).

uma sala, por longos períodos e quando não estejam a ser observadas devem ser mantidas dentro de uma embalagem fechada. As fontes de luz utilizadas para observação destes objectos não devem emitir radiação ultravioleta nem calor, e devem ter uma boa calibração de côr.

2.5. Caso-estudo: a colecção de placas autochrome do Metropolitan Museum of Art

O Metropolitan Museum of Art tem dois grupos de autochrome distintas: um na colecção do *Department of Photographs*, composta por 40 placas, e uma na colecção do estúdio fotográfico composta por 55 placas. Existem ainda duas placas autochrome no *Department of Arts of Africa Oceania and the Americas* (AAOA). A colecção do Department of Photographs (DoP) é composta sobretudo por imagens da autoria de fotógrafos do movimento pictorialista ou *photo-secession*. Uma vez que, tal como o daguerreotipo, o autochrome é uma imagem única (um positivo directo), esta colecção constitui uma das mais importantes de autochromes de valor artístico. Inclui importantes obras de Alfred Stieglitz, Edward Steich, e Heinrich Kühn.

Figura 14: "Miss Mary and Lotte at the Hill Crest", ca.1910. Heinrich Kühn. MMA 2005.100.370

As colecções do estúdio fotográfico e AAOA são compostas de imagens documentais de expedições arqueológicas e antropológicas.

No âmbito da *Research Scholarship* realizada entre 2007 e 2010, estas colecções foram inspeccionadas, relatórios de condição foram realizados, e a colecção do DoP foi tratada por inteiro. Todas as chapas foram limpas, em alguns casos foram feitos tratamentos de restauro, e todas foram armazenadas em embalagens especificamente construídas.

2.6. Bibliografia do capítulo 2

COE, Brian. Colour Photography. 1st. London: Ash & Grant, 1978.

HISTORY OF PHOTOGRAPHY, Volume 18, Number 2, Summer 1994. London/ Washington D.C.: Taylor & Francis Ltd.

KRAUSE, Peter. Preservation of Autochrome Plates in the Collection of the National Geographic Society. Journal of Imaging Science, Volume 29, Number 5, September/ October 1985. Society of Photographic Science and Engineering. pp.182-192.

LAVÉDRINE, Bertrand, and Jean-Paul Gandolfo. "Historical and Technical Investigation of the Autochrome Process and Attempts at Re-creation." Topics in Photographic Preservation 5. American Institute for Conservation, Washington D.C. 1993. pp.138-145.

LAVÉDRINE, Bertrand, and Jean-Paul GANDOLFO. La plaque autochrome : analyses physiques et chimiques, étude de la stabilité des colorants. ICOM Committee for Conservation tenth triennial meeting, Washington, DC, 22-27 August 1993: Preprints. Paris: International Council of Museums Committee for Conservation, 1993.

LAVÉDRINE, Bertrand, Clara von Waldthausen and Lyzanne Gann. "Coatings on Autochrome Plates." Coatings on Photographs: Materials, Techniques and Conservation. Ed. Constance McCabe. Washington, D.C.: AIC, 2005.

LAVÉDRINE, Bertrand, and Jean-Paul Gandolfo. L'Autochrome Lumière. Secrets d'Atelier et Défis Industriels. Paris: Editions CTHS, 2009.

NEWHALL, Beaumont. The History of Photography. New York: The Museum of Modern Art, 1982.

NICKEL, Douglas R. Autochromes by Clarence H. White. Record of the Art Museum, Princeton University, Vol. 51, No. 2, The Art of Pictorial Photography 1890-1925. 1992. pp. 31-37.

PASSAFIUME, Tania. "Photography in Natural Colors: Steichen and the Autochrome Process." Coatings on Photographs: Materials, Techniques and Conservation. Ed. Constance McCabe. Washington, D.C.: AIC, 2005. pp. 314-321.

STIEGLITZ, Alfred. The New Color Photography – A Bit of History. Camera Work, Vol.20. New York: October 1907. pp.20-25.

WAGNER, Sarah, Connie McCabe and Sarah Lemmen. Guidelines ofr Exhibition Light Levels for Photographic Materials. Topic in Photographic Conservation, Volume 9, pp.127-128. AIC: Washington, 2001.

2.7. Índice de figuras do capítulo 2

3. Primeira fase de investigação – testes de envelhecimento acelerado dos seis corantes individuais presentes no ecrã de côr das placas autochrome

Apresentam-se em seguida os seguintes artigos publicados referentes à primeira fase de investigação do projecto:

- "Effects of Low Oxygen Environments in the Light Fading of Six Dyes Present in the Autochrome Color Screen" (2012). Coautor Masahiko Tsukada. *Journal of the American Institute for Conservation*, Fall/ Winter 2012, Vol.51, Number 2. AIC, Washington D.C. pp. 159-174.
- "Behavior of Autochrome Color Screen Dyes Under Anoxic Conditions" (2011). *Topics in Photographic Preservation,* Vol. 14. AIC, Washington D.C. pp. 52-58.
- "Autochrome Research at The Metropolitan Museum of Art: Testing Methodology and Preliminary Results for Anoxia Light-Fading" (2009). *Topics in Photographic Preservation*, Vol. 13. AIC, Washington D.C. pp. 128-136

EFFECTS OF LOW-OXYGEN ENVIRONMENTS IN THE LIGHT FADING OF SIX DYES PRESENT IN THE AUTOCHROME COLOR SCREEN

LUISA CASELLA AND MASAHIKO TSUKADA

ABSTRACT—Because the dyes present in the autochrome color screen are extremely sensitive to light, autochromes are commonly not displayed. The authors investigated the effectiveness of low-oxygen environments in delaying the fading of dyes used in the autochrome process—Tartrazine, Erythrosine B, Rose Bengal, Patent Blue, Crystal Violet, and Flexo Blue. Samples of these colorants were subjected to accelerated light fading in both atmospheric and near-anoxic conditions. The low-oxygen environment was achieved by purging a glass tube with argon gas prior to sealing, maintained with oxygen scavengers, and monitored with indicators capable of detecting oxygen levels above 0.1%. Significant increases in color stability of the dyes were observed in this environment, but a complete halt to the fading process was not achieved.

TITRE—Les effets des environnements à faible teneur en oxygène sur la décoloration de six colorants présents dans les plaques à réseaux autochrome Résumé—À cause de l'extrême sensibilité à la lumière des colorants présents dans leur réseau coloré, les autochromes ne sont généralement pas exposés. Les auteurs ont étudié l'efficacité des environnements pauvres en oxygène pour retarder la décoloration des colorants utilisés dans le procédé autochrome—tartrazine, érythrosine B, rose bengale, bleu patenté, violet cristallisé et bleu flexo. Des échantillons de ces colorants ont été soumis à la décoloration accélérée à la lumière dans des conditions atmosphériques normales ou quasi-anoxiques. L'environnement pauvre en oxygène a été atteint en purgeant le tube en verre contenant les échantillons avec du gaz argon avant le scellage. Il a été maintenu avec des désoxydants et surveillé avec des indicateurs capables de détecter des niveaux d'oxygène supérieurs à 0,1%. Des améliorations significatives de la stabilité de la couleur des colorants ont été observées dans ce milieu, mais un arrêt complet du mécanisme de décoloration n'a pas été atteint.

TITULO—El efecto de ambientes bajos en oxígeno sobre el desvanecimiento—causado por la luz—en seis tintes de la pantalla de color de los autocromos RESUMEN—Debido a que los tintes de las pantallas de color de los autocromos son extremadamente sensibles a la luz, los autocromos normalmente no se exhiben. Los autores investigaron la efectividad de los ambientes con bajo contenido de oxígeno en retardar el desvanecimiento de los tintes utilizados en el proceso del autocromo—Tartrazina, Erythrosina B, Rosa de Bengala, Azul Patente, Violeta Cristal y Azul Flexo. Las muestras de estos colorantes se sometieron a envejecimiento acelerado bajo la luz en dos tipos de ambientes: en atmósfera común y en condiciones cercanas a la anoxia. El ambiente con bajo contenido de oxígeno se logró purgando un tubo de vidrio con gas argón antes de sellarlo, colocando secuestrantes de oxígeno en su interior y monitoreando los niveles con indicadores capaces de detectar hasta 0.1% de oxígeno. Se observó un aumento significativo en la estabilidad de los tintes bajo este ambiente, sin embargo, su proceso de desvanecimiento no se alcanzó a detener por completo.

TÍTULO—Efeitos de atmosferas com baixo oxigênio no esmaecimento à luz de seis corantes presentes na rede de cores do Autochrome RESUMO—Em função dos corantes presentes na rede de cores do autochrome serem extremamente sensíveis à luz, os autochromes normalmente não são expostos. Os autores investigaram a eficácia de ambientes a baixo oxigênio para retardar o esmaecimento de corantes usados no processo de Autochrome – Tartrazina, Eritrosina B, Rosa de Bengala, Azul Patente, Violeta Cristal, e Azul Flexo. Amostras desses corantes foram submetidas a testes acelerados de esmaecimento à luz no ambiente e em atmosferas quase anóxias. O ambiente com baixa quantidade de oxigênio foi conseguido com o preenchimento de um tubo de vidro com gás argônio antes da selagem, mantido com eliminadores de oxigênio, e monitorado com indicadores capazes de detectar níveis de oxigênio maior que 0.1%. Aumentos significativos na estabilidade desses corantes foram observados neste ambiente, mas a suspensão completa do processo de esmaecimento não foi alcançada.

1. INTRODUCTION

In 1903, the French company A. Lumière & Ses Fils patented the autochrome plate, a color screen process that was the first commercially viable method to produce color photographs, manufactured by this company from 1907 to 1935.

Past research has demonstrated that autochrome plates are very sensitive to moisture and heat, as well as to light. Moisture may cause the dyes to dissolve or migrate, heat will cause cracking in the image layer, and light will cause the dyes in the color screen to fade (Krause 1985; Lavédrine et al. 1993; Lavédrine 2009). Within cultural institutions, autochrome plates are considered extraordinarily light sensitive (Wagner et al. 2001). Therefore, there is a general policy of not displaying originals; facsimiles are usually presented instead.

The mechanisms of dye deterioration often depend on the presence of oxygen (Arney et al. 1979; Beltran et al. 2008; Townsend et al. 2008). The effects of anoxic environments on the lightfastness of autochrome dyes was investigated to determine whether applying low-oxygen exhibition systems would allow for safe display of these objects.

1.1 THE AUTOCHROME PROCESS

The autochrome has a layered structure of a glass support covered with a color screen and a photosensitive layer. The color screen had a first varnish layer, made of dammar resin and natural rubber. This varnish layer remained sticky so as to allow adhesion of the color screen filters, which were potato starch grains dyed in red-orange, green, and blue-violet. After the filters were applied onto the first varnish, fine black carbon powder was used to fill the gaps between the starch grains. The filters were then pressed flat by running the plates through a rolling press. A second varnish layer composed of nitrocellulose, castor oil, and dammar resin was applied to protect the starch grains from moisture. Over this color screen layer, a panchromatic silver gelatin emulsion was applied, which constituted the light-sensitive surface (fig. 1).

The autochrome plate was exposed in a camera with the glass and color screen layer facing the subject (fig. 2). Light reflected from the subject reached the photosensitive silver gelatin emulsion only after passing through the color potato-starch filters.

During the first development, the areas affected by the light were reduced to dark metallic silver, resulting in a negative black-and-white image. A bleaching solution then removed the developed metallic silver, leaving only the still-photosensitive silver halides that had not been exposed initially. Next, the plate was exposed to light, affecting the remaining silver salts, and developed a second time. This resulted in a positive black-and-white image. After exposure and processing, photographers often applied a layer of varnish, commonly dammar resin, although other varnishes were also used (see Passafiume 2005). The plates were commonly bound against a cover glass using a paper tape with an adhesive. When the resulting black-and-white positive transparency was viewed in transmitted light, the minute color filters embedded in the color screen produced the effect of a positive image in natural colors.

1.2 PAST ANOXIA RESEARCH AND RATIONALE

It has been known since the end of the 19th century that some colorants are more stable in light if kept in oxygen-free conditions. In 1888, the Russell and Abney Report cited lightfastness test results for a variety of watercolor materials, demonstrating that, in the absence of oxygen, the majority of colorants tested were seen to fade at a much slower rate or not at all. Subsequent studies on the effects of anoxia have established that individual dyes react differently when exposed to light under anoxic conditions. For example, textiles dyed with Prussian Blue will be adversely affected by the absence of oxygen, undergoing fading by photoreduction (Rowe 2004).

Significant research projects on anoxia applied to artists' color materials are currently underway at the Getty Conservation Institute and Tate Britain (Beltran et al. 2008; Townsend et al. 2008), and anoxic enclosures for objects on display have been successfully employed in the preservation of museum objects (Maekawa 1998). However, research on the specific application of anoxic environments to the display of photographic materials has been limited.

At the beginning of this research, the anoxic light fading behavior of the six specific dyes used to create the autochrome color screen—Tartrazine, Erythrosine B, Rose Bengal, Patent Blue, Crystal Violet, and Flexo Blue (Lavédrine et al. 1993,

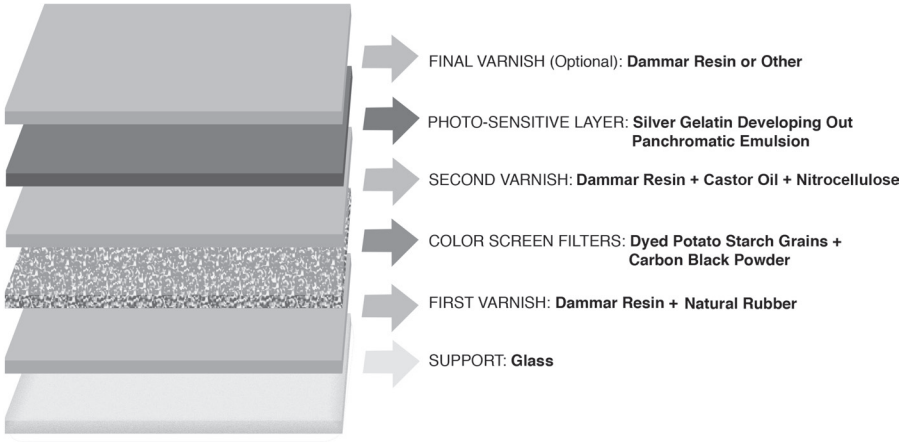

Fig. 1. Autochrome layered structure. Illustration by Guida Casella.

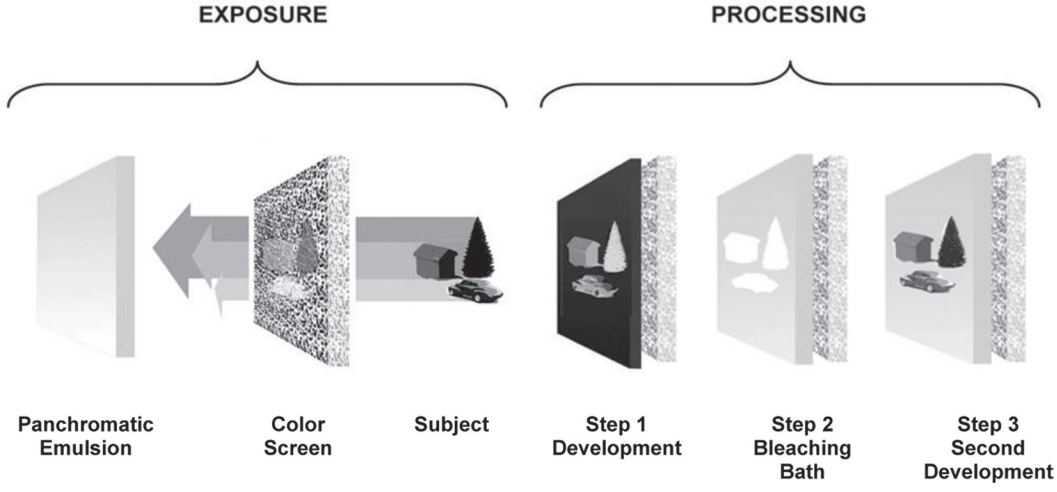

Fig. 2. Exposure and processing steps in the production of autochromes. Illustration by Guida Casella.

Lavédrine 2009)—had not been established insofar as a literature search and extensive consultation with colleagues could determine. In this project, the influence of oxygen in the light fading of each dye was investigated to determine whether there is a protective effect that would allow for the exhibition of autochromes under anoxic conditions, and to establish whether the colorants have different fading rates in this environment that might lead to tonal shifts in the image.

2. EXPERIMENTAL

Samples produced for an accelerated light aging test consisted of potato starch grains dyed with each of the six dyes, between varnish layers, on a glass support. In addition, samples with the varnish layers alone on a glass support were produced. All samples were prepared following historic formulations provided by Bertrand Lavédrine, director of the Centre de recherche sur la conservation des collections in Paris, France, and is

Table 1.
Dyes used in the autochrome color screen

Filter	Dye	CI Number	Other Names	Appearance
Red-orange	Erythrosine B	45430	Acid Red 51	Red
	Rose Bengal	45440	Acid Red 94	Magenta
	Tartrazine	19140	Acid Yellow 23	Yellow
Green	Patent Blue	42051	Acid Blue 3	Blue
	Tartrazine	19140	Acid Yellow 23	Yellow
Blue-violet	Crystal Violet	42555	Basic Violet 3	Purple
	Flexo Blue	42025	Basic Blue 1, Setoglaucine	Blue

Table 2.
Historic formulation of dye solutions to tint the color screen filters

Red-orange filter	Green filter	Blue-violet filter
Distilled water – 100 ml	Distilled water– 100 ml	Distilled water – 100 ml
Erythrosine B – 14.5 g	Ammonia – 9 g	Crystal Violet – 7 g
Rose Bengal – 2.6 g	Tartrazine – 21 g	Flexo Blue – 1 g
Tartrazine – 19.7 g	Patent Blue – 10 g	
	Sodium Sulfate – 21 g	

widely regarded to be one of the leading experts on autochrome research. As the purpose of the test was solely to study the color screen, the samples did not have a photosensitive layer.

2.1. SAMPLE PREPARATION

2.1.1 Selection of Starch Grains

The potato starch grains that form the autochrome color screen range from 10 to 20 μm in diameter. Historically, to retrieve grains of homogeneous dimensions, the potato starch was separated by flotation and sieved through calibrated nets. Since image resolution was not critical for the present experiment, only one stage of separation by flotation was carried out to retrieve a sufficiently homogeneous group of grains. Into a large beaker filled with 2 L of distilled water, 75 g of commercially available potato starch was stirred and allowed to settle. After 15 minutes, the larger grains were deposited in the bottom, while the smaller particles remained in suspension. Using a plastic tube, the intermediate layer of starch was siphoned and filtered through Whatman filter paper. The grains were rinsed in ethanol and air-dried.

2.1.2 Tinting of Starch Grains

The red-orange, green, and blue-violet autochrome color filters were produced by a combination of the six dyes presented in table 1. Malachite Green Orthochlorinated, with the Color Index (CI) number 42025, will be referred to in this article as Flexo Blue, so as not be confused with Malachite Green (CI 42000). Other dyes, such as Malachite Green Meta-Chlorinated and Diiodofluorescein are found in the color screen as dye impurities (Lavédrine 2009) and were therefore not tested in this study.

The historic recipes for the dye solutions are shown in table 2. In the solution for the green filter, ammonia and sodium sulfate were added to increase the pH and improve the adsorption of these dyes onto the starch grains.

In order to observe the individual lightfastness of each dye, the starch grains were tinted with each of the six colorants rather than in the three color mixtures. For example, to produce the solution of Erythrosine dye used for the experiment, 14.5 g of dye was diluted in 100 ml of distilled water. The dye Tartrazine, which was historically used in two different concentrations (in the red-orange

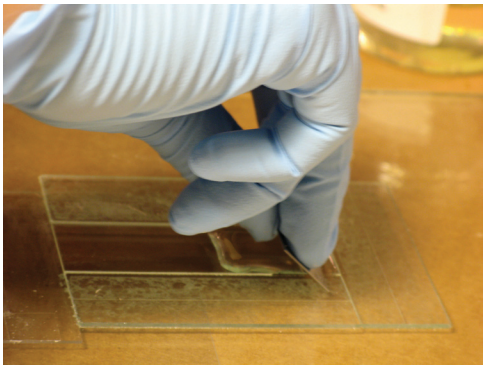

Fig. 3. Applying varnish layer using a spreader.

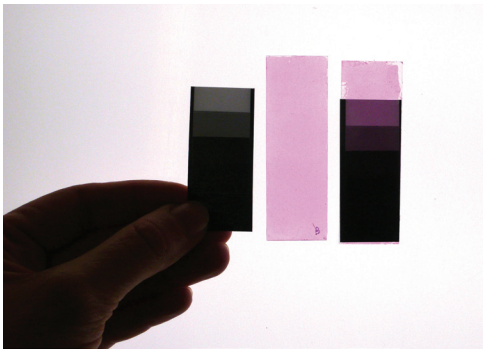

Fig. 4. Grayscale, autochrome sample, and autochrome sample with grayscale overlay (*l–r*), transmitted light.

and green filters), was diluted, 20.35 g in 100 ml of distilled water.

An approximate amount of 2.3 g of each dye solution at room temperature was added to 3 g of starch and stirred until no white starch grains were visible. The dye solutions of Crystal Violet and Flexo Blue were mixed with the starch while being heated at 30°C in a double boiler, following the instructions in the historical recipe. The tinted grains were strained through Whatman filter paper and air-dried.

2.1.3 Preparation of Varnish Layers

Historic recipes were used to prepare the two varnishes present in the autochrome color screen. Dammar resin was employed to prepare both varnish layers: 9.6 g of resin were dissolved in 100 ml of ethyl acetate for 24 hours, stirring occasionally. At this point there was resin in solution and a white residue in the bottom of the jar. This insoluble residue was recovered with Whatman filter paper, rinsed in ether and dried, and used for the first varnish. The filtered dammar resin solution was used for the second varnish.

For the preparation of the first varnish, 1.5 g of unvulcanized natural rubber was dissolved in 100 g (87 ml) of toluene. The recovered residue of dammar resin insoluble in ethyl acetate, mentioned previously, was then dissolved in toluene at 10% (w/v). Of this solution, 5.6 ml was added to the dissolved unvulcanized rubber.

For the second varnish, 2.4 g of nitrocellulose was added to the filtered solution of dammar resin and stirred until complete dissolution, which took 15 days. Subsequently, 1.5 g (1.44 ml) of castor oil was added.

2.1.4 Sample Assembly

For the sample support, microscope glass slides were individually cleaned with ethyl alcohol and let dry. A layer of the first natural-rubber–based varnish was applied using a spreader (fig. 3), and let dry for about 18 hours. The spreader was used to maintain the same thickness of varnish from sample to sample. Historic autochrome plates had a varnish layer thickness of 5 µm (Krause 1985), which would be extremely difficult to reproduce. The test samples' varnish layer thickness was ca. 50 µm.

The potato starch grains dyed with each of the six colorants were applied with a soft brush in a stippling motion to this sticky varnish layer, taking care not to abrade the very delicate varnish. A layer of the second nitrocellulose-based varnish was applied using a spreader.

The samples of varnish layers without dyed potato starch were prepared in a similar procedure. For each dye and for the varnish samples, ten duplicates were created, five to be tested under near-anoxic conditions and five in normal air environment, for a total of 70 samples. An additional set of the samples was also prepared to serve as the control (not exposed to light).

2.2 COLOR MONITORING

Prior to and after light exposure, transmission spectral data was collected using a Varian Cary 50 Bio UV-Vis Spectrophotometer. The

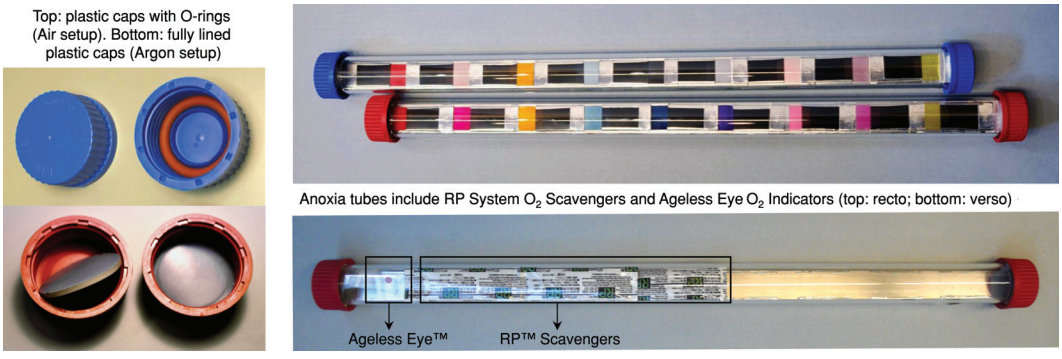

Fig. 5. Test setup for light exposure of autochrome samples. The samples were closed in sealed tubes that had been filled with either air or argon. Argon-filled tubes also included oxygen scavengers (RP System) and an oxygen indicator (Ageless Eye) facing the back of the tubes.

instrument uses a Xenon flash lamp as a source, and a 1 cm^2 silicon photodiode as a detector. Spectra are acquired by scanning monochromatic light (with a spectral bandwidth of 1.5 nm) over the sample with a user-selected step size and averaging times. In this study, the measurements were done at 5 nm intervals between 360 and 830 nm, and by averaging three readings in each area. Polyester sheet overlays were used to ensure consistency of the measurement locations before and after light aging.

2.3 TESTING SETUP

The test setup consisted of samples assembled on aluminum strips, overlaid by density step wedges to create a gradation of light exposure. For each sample, one area was left fully exposed and another fully protected from light using 3M 425 aluminum tape. The placement of the samples was made in a random manner on each strip, so that, in the event of one or more of the tubes experiencing oxygen ingress, part of the data could still be retrieved.

The aluminum strips, with nine samples each, were placed inside custom-made glass tubes manufactured with Corning Pyrex 7740. The tubes had threaded ends to fit plastic caps. Achieving a successful seal involved several failed attempts, due to the permeability of the caps used initially and difficulty in aligning them adequately. For the final setup, the caps used had a thick polytetrafluoroethylene (PTFE) lining (fig. 5). Thread seal PTFE tape was applied on the thread of each glass tube.

The low-oxygen tubes were placed inside a glove bag and filled with argon gas humidified to ca. 45%RH. Argon was chosen for its ready availability at The Metropolitan Museum of Art (the Met) due to its use for other anoxic packages. The relative humidity level was based on actual conditions in the photography galleries of the museum, to match those of the Air sample group.

The humidity of the argon gas was adjusted before introducing it into the tubes by mixing dry argon gas directly from a gas cylinder with moist argon gas that had been passed through a water trap filled with distilled water. During the purging of each tube, the oxygen concentration was lowered to less than 500 ppm, which was monitored with an oxygen analyzer (Illinois Instrument, Inc. Model 911). Three RP-K System scavenger pouches were placed inside each tube to absorb any residual oxygen. One Ageless Eye indicator within the tube monitored the oxygen concentration during light exposure.

The group of samples to be exposed to light under normal air conditions was prepared in an identical setup in glass tubes, sealed at 45%RH without purging with argon and without oxygen scavengers. A third set of samples was kept in the dark, inside an aluminum foil pouch, under ambient conditions, as a control.

2.4 ACCELERATED FADING

The tubes were wrapped in Marvel Seal 360 film (aluminum foil laminated between polyethylene and nylon film) to protect the samples from light, and

Table 3.
Light exposure values

	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6
Optical Density of Step Wedges (Vis)	Fully Exposed	0.59	1.03	1.72	1.84	Totally Covered
Transmission (%)	100	25.7	9.33	1.91	1.45	0
Light Dose (Mlx·hrs)	8.3	2.1	0.77	0.16	0.12	0
Equivalent Days of Exposure at 2000 lx, 9 hrs per day	460	118	43	9	7	0
Equivalent Days of Exposure at 500 lx, 9 hrs per day	1842	473	172	35	26	0

transported to the Image Permanence Institute at Rochester Institute of Technology, where they were placed in a light fading unit using Sylvania F40/CWX fluorescent lamps for 54 days. This lamp emits almost no fraction of light below 400 nm; the illuminance at the sample surface was 6400 lx. The Pyrex 7740 used for the glass tubes in this experiment transmits more than 90% of the light in the range between 350 and 2000 nm. The area of full exposure was subjected to close to 8.3 Mlx•h, which would be comparable to that of display in a light box emitting 2000 lx for 9 hours a day over a period of approximately 14 months. The optical density and transmittance of the step wedges and corresponding light doses of the remaining areas are summarized in table 3.

In the light fading unit, the lamps moved while the samples stayed in place to ensure the homogeneity of the light exposure of all the samples. Constant ventilation prevented heat build-up; temperature was maintained at 25°C, measured on the surface of the glass tubes using a Raytek Raynger ST non-contact thermometer.

3. RESULTS AND DISCUSSION

After exposure in the light fading unit, the experiment tubes were wrapped in Marvel Seal 360 film and transported back to the Met. One of the low-oxygen tubes had a leak, causing one of the five Erythrosine B samples to be disregarded in the results. (The remaining materials tested on this faulty tube are not being discussed in the present article.) Spectrophotometric readings were taken, measuring the six areas of graded exposure of each sample.

3.1 DYE SAMPLES

3.1.1 Color Change Observations

To evaluate the color change in the samples, the three coordinates of CIE L⋆a⋆b⋆ were obtained using the spectrophotometer's software with the settings of D50 illuminant with a 2° observer, and the color difference, ΔE, from the control (samples not exposed to light) was calculated according to CIE 1976, which was the standard used in most of the references consulted. The resulting ΔE value obtained for each of the five sample duplicates was averaged and is summarized in table 4. The standard deviation values are at times quite high, denoting a high degree of variation among the samples, possibly due to the heterogeneity of the dye application inherent to the sample preparation method.

Figure 6a–f illustrates the average ΔE values for each dye in relation to the light exposure of each area. Note that change has occurred in the sample areas that were fully protected from light (area 6), which suggests that light exposure is not the only agent of deterioration for these dyes.

We can observe that low-oxygen conditions demonstrate a clear benefit for Erythrosine B and Rose Bengal in all areas of exposure. Crystal Violet clearly showed less change in the areas above 2.1 Mlx•h of exposure, but the results are ambiguous at lower levels of light exposure.

Table 4.
Average of the ΔE values (standard deviations in parentheses) of the five samples of each set (except Erythrosine B in low-oxygen conditions, with four samples). Refer to table 3 for corresponding light doses.

		Area 1 8.3 Mlx•h	Area 2 2.1 Mlx•h	Area 3 0.77 Mlx•h	Area 4 0.16 Mlx•h	Area 5 0.12 Mlx•h	Area 6 No light exposure
Air	**Erythrosine B**	36.4 (1.7)	34.3 (1.5)	25.7 (2.1)	14.8 (4.4)	13.5 (5.0)	13.0 (5.9)
	Rose Bengal	33. 8 (2.4)	33.4 (0.7)	25.6 (1.3)	13.4 (1.5)	12.1 (1.8)	11.3 (2.3)
	Tartrazine	0.9 (0.6)	0.7 (0.4)	1.6 (0.6)	1.9 (0.4)	1.3 (0.9)	1.1 (0.7)
	Flexo Blue	14.1 (1.5)	7.2 (1.4)	4.1 (0.8)	2.3 (0.7)	2.2 (1.1)	3.8 (1.7)
	Patent Blue	8.6 (4.5)	2.9 (0.4)	1.9 (0.2)	1.6 (1.3)	2.0 (1.4)	1.1 (0.1)
	Crystal Violet	22.7 (1.3)	11.2 (7.5)	3.4 (2.3)	2.3 (1.2)	1.7 (1.3)	2.9 (1.6)
Argon	**Erythrosine B**	9.9 (3.8)	3.4 (2.2)	0.9 (0.8)	0.6 (0.5)	1.3 (1.0)	2.6 (1.4)
	Rose Bengal	6.7 (1.9)	1.8 (0.9)	1.5 (0.7)	2.2 (0.2)	2.6 (1.1)	2.0 (1.7)
	Tartrazine	0.8 (0.4)	0.6 (0.6)	3.1 (2.2)	3.7 (1.9)	3.3 (2.0)	1.1 (0.3)
	Flexo Blue	12.7 (1.2)	5.3 (0.6)	3.6 (1.0)	5.4 (1.0)	4.4 (2.3)	4.8 (1.4)
	Patent Blue	4.6 (1.1)	2.3 (0.8)	2.6 (0.6)	2.5 (1.3)	2.8 (0.8)	3.3 (1.0)
	Crystal Violet	6.9 (3.4)	3.1 (2.3)	2.3 (1.5)	2.3 (0.9)	2.8 (1.7)	3.8 (3.2)

Tartrazine, Flexo Blue, and Patent Blue showed relatively low degrees of change in general. Tartrazine appeared to have higher degrees of change under low-oxygen conditions between 2.1 Mlx•h and 120 klx•h of light exposure, as did Flexo Blue and Patent Blue between 160 and 120 klx•h of exposure. Patent Blue showed a slight benefit under low-oxygen at the maximum level of light exposure. However, it is possible that in these cases the degree of change is so low that the differences might fall within the margin of error of our measurements, given the high standard deviations.

Table 5 summarizes the L⋆a⋆b⋆ values for the areas fully exposed to 8.3 Mlx•h of light.

3.1.2 Spectral Curve Observations

Figures 7 to 12 show the spectral curve of each dye in area 1, the area fully exposed to 8.3 Mlx•h of light. Erythrosine B and Rose Bengal, both xanthene dyes, showed similar changes with light exposure. The samples exposed under normal environmental oxygen conditions show an increase in light transmission in the 500–550 nm region and decrease in the 400–460 nm region, especially at exposures between 8.3 Mlx•h and 770 klx•h (areas 1 to 3), when compared to the control. At exposures between 160 and 0 klx•h (areas 4 to 6), the same tendency was observed, but there was less change. The change that occurred in the area that was covered (area 6)

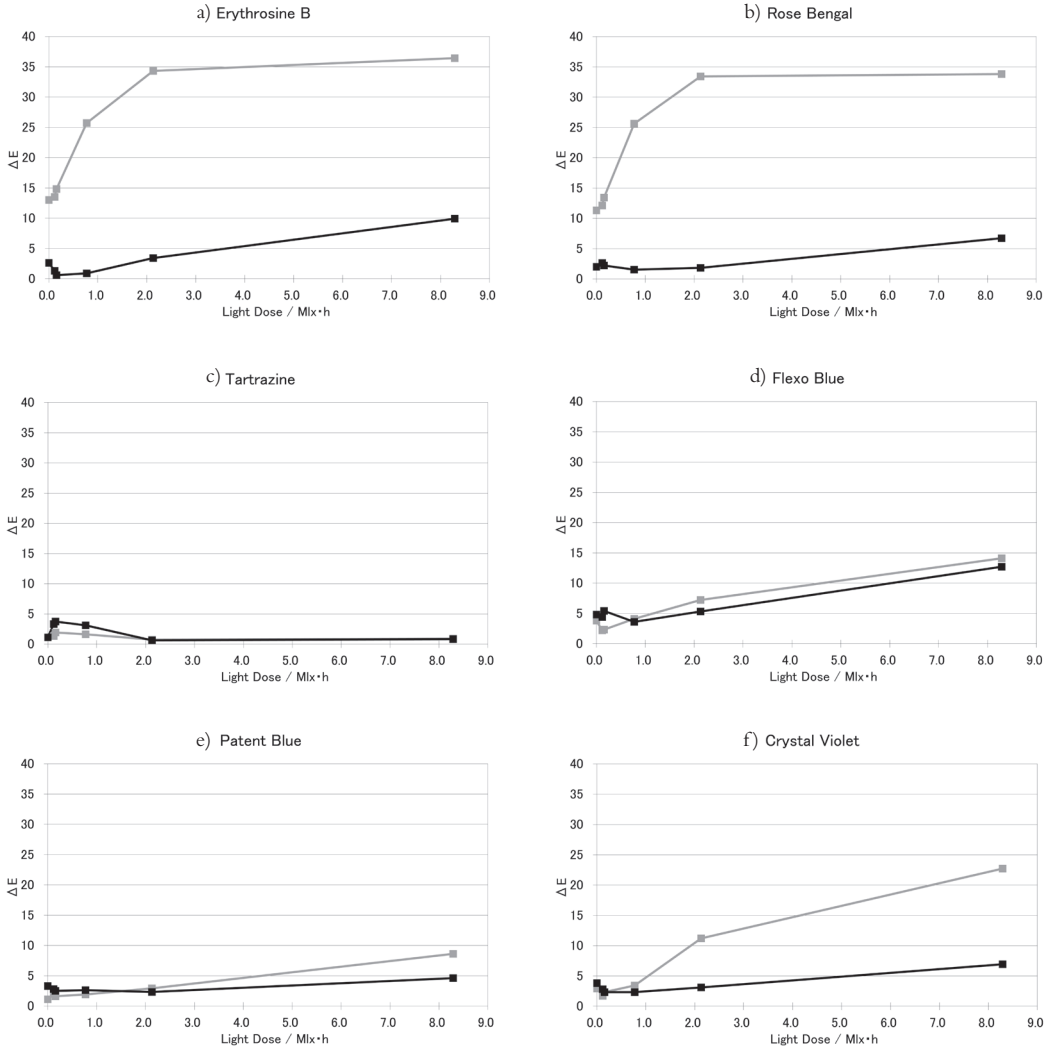

Fig. 6. Plot of the ΔE values measured in the six areas of each sample, representing color changes from exposure to the six light doses in the areas described in table 3. Results shown after light exposure in air (gray curves) and in near-anoxic conditions (black curves) for a) Erythrosine B, b) Rose Bengal, c) Tartrazine, d) Flexo Blue, e) Patent Blue, f) Crystal Violet.

suggests that light exposure was not the only agent affecting the color of these dyes. The samples exposed under near-anoxic conditions showed lower increase in the 500–550 nm region and a very slight decrease below 460 nm. Erythrosine B samples in air presented a significant shift towards +L* (lighter), and also towards green (-a*) and yellow (+b*), changes that were less under low-oxygen conditions (table 5).

In both argon and air environments, the change in Tartrazine, a monoazo dye, was not significant, consistent with past findings that Tartrazine is the most stable of the autochrome dyes (Lavédrine et al. 1993). However, a change is observed towards the violet region of the curve (below 430 nm) in the samples exposed in air to more than 770 klx•h (areas 1 to 3). This is likely related to a change occurring

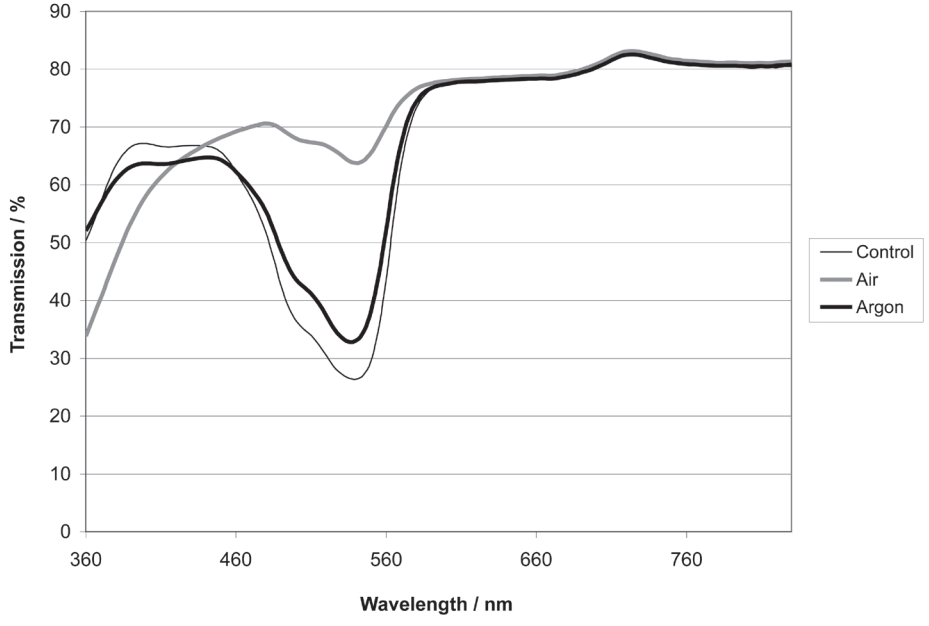

Fig. 7. Visible transmission spectra of Erythrosine B samples in area 1 before light exposure (control) and after 54 days of exposure to fluorescent lights in air or in argon at 45%RH (8.3 Mlx•h).

Table 5.
L*a*b* values of all dye samples in area 1, exposed to 8.3 Mlx•h

Dye	Condition	L*	a*	b*
Erythrosine B	Control	76.3	38.5	-9.9
	Air	87.4	6.2	2.6
	Argon	79.0	30.2	-5.4
Rose Bengal	Control	75.9	30.5	-17.3
	Air	87.3	4.7	1.3
	Argon	77.9	26.0	-12.7
Tartrazine	Control	90.3	-9.4	31.2
	Air	90.3	-9.8	31.1
	Argon	89.8	-9.4	31.7
Flexo Blue	Control	70.9	-23.5	-20.4
	Air	75.7	-18.5	-8.3
	Argon	74.5	-19.7	-8.8
Patent Blue	Control	75.3	-23.5	-18.6
	Air	76.0	-18.3	-9.9
	Argon	75.2	-19.8	-16.0
Crystal Violet	Control	61.7	17.2	-36.2
	Air	69.6	4.0	-19.5
	Argon	63.0	14.6	-31.0

in the varnish layer, which will be discussed in section 3.2.

For Flexo Blue and Patent Blue, both triphenylmethane dyes, there was a similar and noticeable change in the samples exposed in argon and in normal air environments, in the area of full exposure (area 1). Spectral features were maintained to a certain extent, but the light transmission increased in the 550–700 nm region and decreased in the 440–520 nm region, compared to the control. All the samples showed shifts towards red and yellow, and towards +L* (lighter) for Flexo Blue (table 5). For both dyes, these changes were greater in the samples exposed to normal air environment. A decrease in the spectral curve was noted in the violet region similarly to Tartrazine, in the areas exposed to more than 770 klx•h (areas 1 to 3).

In the samples with Crystal Violet, also a triphenylmethane dye, there is a noticeable change in the areas exposed to more than 2.1 Mlx•h (areas 1 and 2), both under argon and normal air conditions. Those in the last group have a more pronounced shift towards green and yellow, as well as fading. In all areas of the samples exposed under low-oxygen (argon)

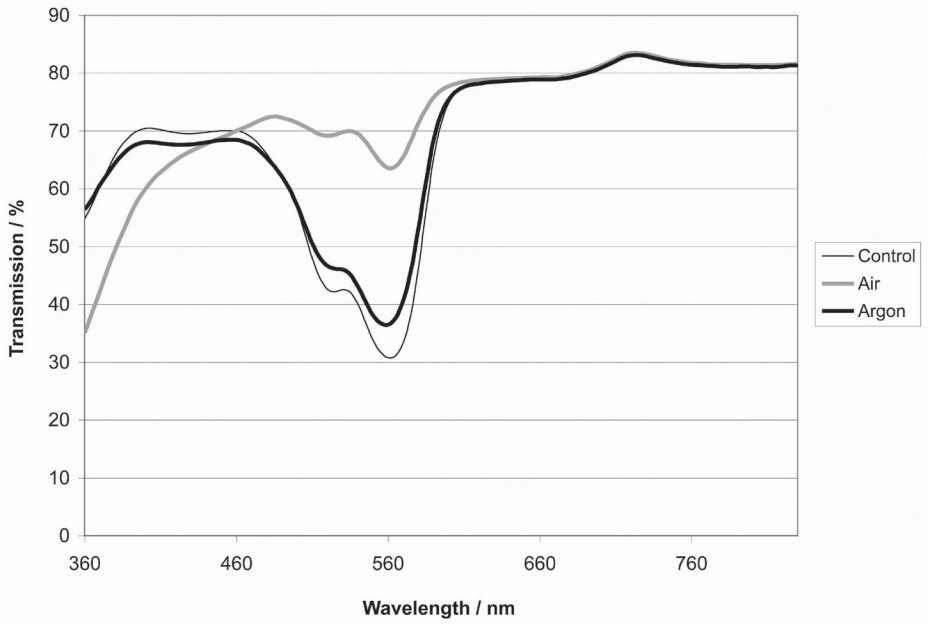

Fig. 8. Visible transmission spectra of Rose Bengal samples in area 1 before light exposure (control) and after 54 days of exposure to fluorescent lights in air or in argon at 45%RH (8.3 Mlx•h).

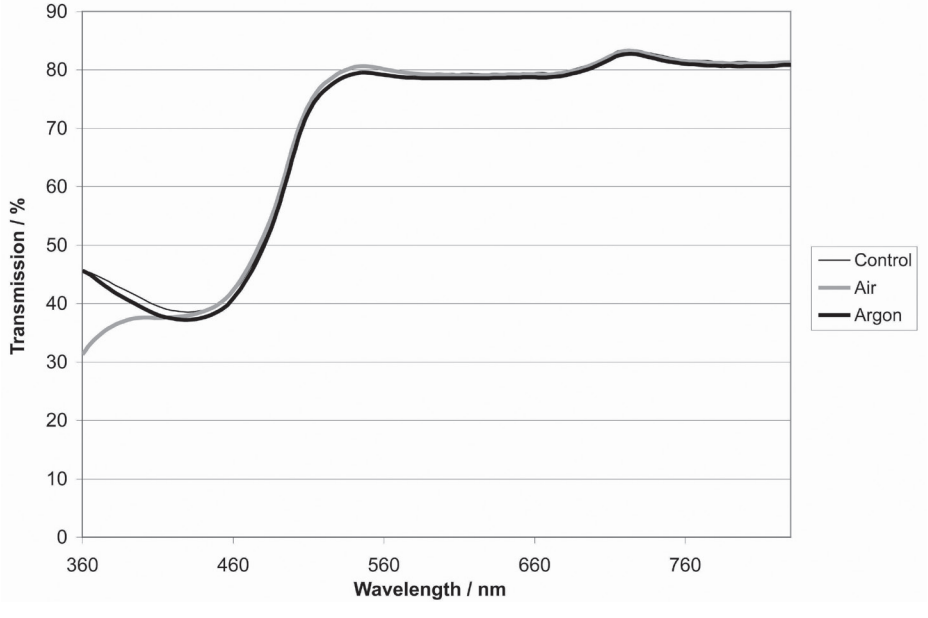

Fig. 9. Visible transmission spectra of Tartrazine samples in area 1 before light exposure (control) and after 54 days of exposure to fluorescent lights in air or in argon at 45%RH (8.3 Mlx•h).

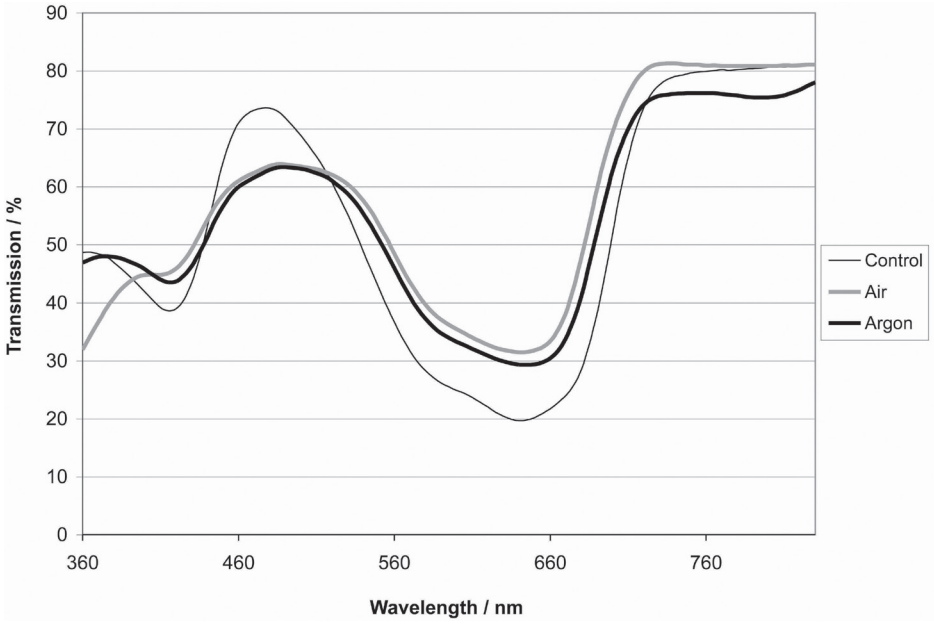

Fig. 10.Visible transmission spectra of Flexo Blue samples in area 1 before light exposure (control) and after 54 days of exposure to fluorescent lights in air or in argon at 45%RH (8.3 Mlx•h).

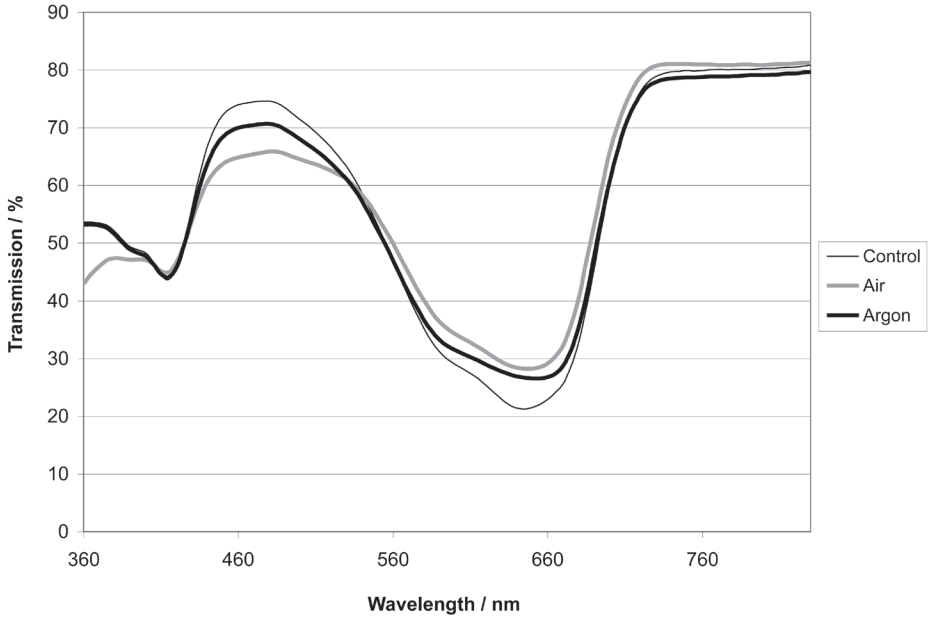

Fig. 11.Visible transmission spectra of Patent Blue samples in area 1 before light exposure (control) and after 54 days of exposure to fluorescent lights in air or in argon at 45%RH (8.3 Mlx•h).

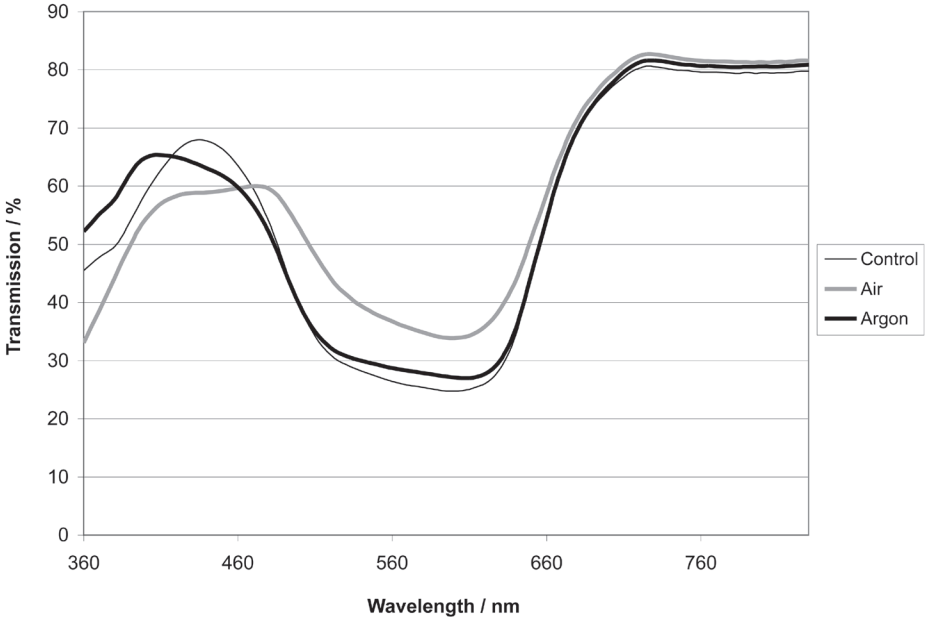

Fig. 12. Visible transmission spectra of Crystal Violet samples in area 1 before light exposure (control) and after 54 days of exposure to fluorescent lights in air or in argon at 45%RH (8.3 Mlx•h).

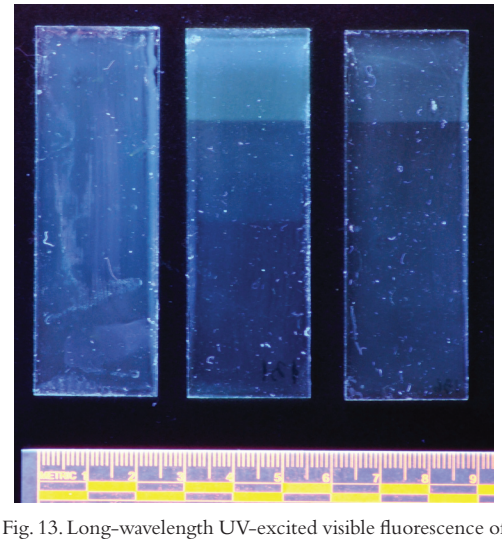

Fig. 13. Long-wavelength UV-excited visible fluorescence of varnish samples: control, exposed to light in air, and exposed to light in argon (*l*–*r*).

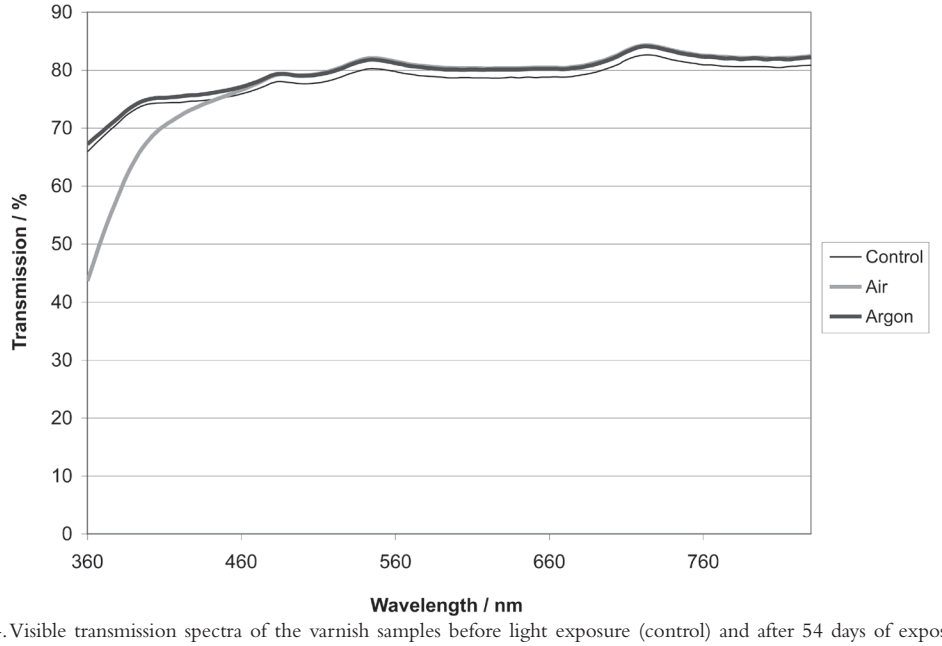

Fig. 14. Visible transmission spectra of the varnish samples before light exposure (control) and after 54 days of exposure to fluorescent lights in air or in argon at 45%RH (8.3 Mlx•h).

conditions, we observed a slight increase of the light transmission below 430 nm towards the ultraviolet region.

3.2 VARNISH SAMPLES

The optical density values of the varnish layers after light exposure showed negligible change. As observed under the microscope, there were no signs of physical deterioration of the samples, such as cracking noted in previous accelerated aging tests of these materials (Lavédrine et al. 1993, see especially p.279). However, inspection under long wave ultra-violet light revealed a cloudy appearance in the samples (figure 13). The degree of change visible in the sample exposed to light in low-oxygen conditions is lower than that of the samples exposed in normal environmental oxygen levels. Figure 14 shows the transmission spectra of the varnish samples on the area of full exposure (8.3 Mlx•h, area 1). The sample exposed under low-oxygen environment does not show significant change compared to the control, while the sample exposed in a normal air environment showed a noticeable decrease of light transmission below around 450 nm towards the ultraviolet region. This same phenomenon was observed quite clearly in the glass-supported samples of Tartrazine, Flexo Blue, and Patent Blue exposed in a normal air environment, changing the spectral feature from the control. The remaining dye samples exposed in a normal air environment also show a decrease of light transmission in this region, but this is less noticeable because the original shape of the curves had lower transmissions in this region of the spectrum. From the spectral curve on figure 14, we can assume that these changes were due to the effect in the varnish layer.

4. CONCLUSIONS

The results of the tests presented here demonstrate a beneficial effect of low-oxygen environments in decreasing the fading rate of the dyes present in the autochrome color screen at levels of light exposure above 2.1 Mlx•h (areas 1 and 2 of the test). A low-oxygen environment will not, however, completely stop the fading of the colorants in this system. At lower levels of light exposure, below 770 klx•h (areas 3 to 6), the benefit of the low-oxygen environment became ambiguous, probably due to the heterogeneity of the dyed grain distribution

in the samples that sometimes caused a significant color difference within the same set of samples. It is important to note that the low-oxygen environment was reliant on oxygen indicators capable of detecting levels of oxygen as low as 0.1%. This low level of oxygen may yet be sufficient to cause the oxidative fading reactions of some of the dyes present in the autochrome system.

The experimental results show change in the areas of the samples that were fully protected from light (see table 4). The extent of this change, especially in Erythrosine B and Rose Bengal, appears to be greater than what can be attributed to heterogeneity of the grain distribution on the samples, even though high levels of standard deviation were observed when averaging the readings of the five samples of each group. These results suggest that light exposure is not the only agent of deterioration acting upon the dyes.

The experiment also showed that the light fastness and the extent of the beneficial effect of low-oxygen environments in decreasing the fading rate are different depending on the dyes. This implies that in real-world conditions, autochromes exposed to light may display a color imbalance as mentioned in the literature (Lavédrine, B. 2009). Although we know the ratio of each dye in each color filter, it is difficult to predict the direction of the color shift in real autochromes on view based only on the results of the present study, warranting further investigation to be conducted in the next phase of the project.

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REFERENCES

Arney, J. S., A. J. Jacobs, and R. Newman. 1979. The influence of oxygen on the fading of organic colorants. *Journal of the American Institute for Conservation* 18:108–17.

Beltran, V., J. Druzik, and S. Maekawa. 2008. An extended investigation of the influence of oxygen on color fading. Poster presented at the ICOM-CC 15th Triennial Conference, New Delhi, 22–26 September 2008. Abstract in *ICOM Committee for Conservation Preprints*, ed. J. Bridgland. Paris: ICOM. 280.

Krause, P. 1985. Preservation of autochrome plates in the collection of the National Geographic Society. *Journal of Imaging Science* 29(5): 182–92.

Lavédrine, B. 2009. *L'Autochrome lumière. Secrets d'atelier et défis industriels*. Paris: Editions CTHS.

Lavédrine, B., J. P. Gandolfo, and J. M. Subsielles. 1993. La plaque autochrome: Analyses physiques et chimiques, étude de la stabilité des colorants. In *ICOM Committee for Conservation Preprints*. 10th Triennial Meeting, Washington, D.C. Paris: ICOM. 1:275–80.

Maekawa, S., ed. 1998. *Oxygen-free museum cases*. Los Angeles, Calif.: J. Paul Getty Trust.

Passafiume, T. 2005. Photography in natural colors: Steichen and the autochrome process. In *Coatings on photographs: Materials, techniques and conservation*, ed. C. McCabe. Washington, D.C.: American Institute for Conservation of Historic and Artistic Works.

Rowe, S. 2004. The effect of insect fumigation by anoxia on textiles dyed with Prussian Blue. *Studies in Conservation* 49(4): 259–70.

Russell, W. J., and W. de W. Abney. 1888. *Report to the Science and Art Department of the Committee of Council on Education, on the action of light on watercolours*. London: Great Britain Education Department, HMSO.

Townsend, J., S. Hackney, J. Thomas, and A. Lerwill. 2008. The benefits and risks of anoxic display for colorants. *Conservation and access*, ed. D. Saunders, J. H. Townsend, and S. Woodcock. London: International Institute for Conservation of Historic and Artistic Works. 76–81.

Wagner, S., C. McCabe, and B. Lemmen. 2001. Guidelines for exhibition light levels for photographic materials. *Topics in Photographic Preservation*, Vol. 9, comp. S. Wagner. Washington, D.C.: American Institute for Conservation of Historic and Artistic Works. 127–28.

MATERIALS

Ageless Eye oxygen indicators, RP-K oxygen scavengers
Mitsubishi Gas Chemical America
655 Third Ave., 24th Floor
New York, NY 10017
Tel: (212) 687-9030
Fax: (212) 687-2810
www.mgc-a.com

Corning Pyrex 7740 glass tubes
Kimble/Kontes, Kimble Chase LLC
1022 Spruce St.
Vineland, NJ 08362-1502
Tel: (800) 682-6644
Fax: (856) 692-6644
www.kimble-chase.com

Crystal Violet CI 42555 (Basic Violet 3); SIAL sold through Sigma-Aldrich
Flexo Blue CI 42025 (Basic Blue 1); name given by supplier: Rhoduline Blue 6G; Salor sold through Sigma-Aldrich
Patent Blue CI 42051 (Acid Blue 3); name given by supplier: Patent Blue V Calcium Salt; Fluka sold through Sigma-Aldrich
Rose Bengal CI 45440 (Acid red 94)
Tartrazine CI 19140 (Acid Yellow 23); Fluka sold through Sigma-Aldrich
Sigma-Aldrich
3050 Spruce Street
St. Louis, MO 63103
Tel: 800-325-3010
Fax: 800-325-5052
www.sigmaaldrich.com

Erythrosine B CI 45430 (Acid Red 51)
Name given by supplier: Erythrosin, Bluish (Iodin Eosin)
National Aniline & Chemical Co. (company no longer exists)

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BEHAVIOR OF AUTOCHROME COLOR SCREEN DYES UNDER ANOXIC CONDITIONS

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Presented at the PMG session of the 2010 AIC Annual Meeting in Milwaukee, Wisconsin

ABSTRACT - Ongoing research at The Metropolitan Museum of Art in New York has focused on the possible application of anoxic environments in preventing light-fading of autochrome color screen dyes during exhibition The methodology used in the experiment was presented during the 2008 PMG Winter Meeting at the Center for Creative Photography in Tucson, AZ (Casella 2009). The current paper presents the results of the experiment. The project tested the six dyes present in the autochrome color screen. Test samples were prepared of each of the dyes. The anoxic setup was achieved by using sealed glass tubes. A group of samples was purged with argon; a second group was sealed under atmospheric oxygen conditions. The samples were exposed to light in a fading unit at the Image Permanence Institute in Rochester, NY. Spectrophotometric data was collected before and after light fading. The results show that the fading rate of all of the individual dyes is lower under anoxic conditions.

1. INTRODUCTION

The autochrome represents the first commercially viable color photographic process, produced from 1907 to 1935 (Lavédrine 2009). It is a transparent positive on a glass support and was viewed by projection or transmitted light. Most deterioration and damage characteristics found in autochromes, such as the breakage of the support, mirroring of the silver image, glass deterioration, image layer delamination, or formation of green staining, are more or less understood (Krause 1985). However, the causes of commonly observed color shifts in the dye layer and discolorations are not entirely clear. They may have occurred during processing or over time.

Research on autochromes has been led by the French conservation scientist Bertrand Lavédrine. Light fading tests he conducted confirmed the poor light fastness of the dyes in the color screen layer. As a result, the current policy of the majority of cultural institutions, including The Metropolitan Museum of Art, has been *not* to display original autochrome plates, which are considered "*extraordinarily light-sensitive"* (Wagner et al. 2001), but to show facsimiles or simulacra.

Lavédrine identified six dyes in the color screen layer, which were used consistently during the entire production period from 1907 to 1935: Erythrosine B (C.I. 45430), Rose Bengal (C.I. 45440), Tartrazine (C.I. 19140), Patent Blue (C.I. 42051), Crystal Violet (C.I. 42555) and Setoglaucine or Flexo Blue (C.I. 42025). The dyes were mixed to form red-orange, green and blue-violet solutions with which potato starch grains were tinted to create the color screen filters.

Past research has shown that certain colorants either do not fade at all or fade less if exposed to light under anoxic conditions (Arney et. al 1979; Beltran et al. 2008; Townsend et al. 2008).

However, some colorants will fade more rapidly in the absence of oxygen (Rowe 2004), which determines the need to test each individually. At the beginning of this project, there was no existing research on the light-fading behavior under anoxic conditions of the six dyes used in the autochrome process. The first phase of research consisted of a light-fading test of each individual dye.

2. LIGHT FADING EXPERIMENT

For each of the six dyes, four groups of samples were prepared following the historic dye concentrations and varnish recipes. The first group consisted of dyed potato starch grains encased between two varnish layers, applied to a glass support. This sample set tested the behavior of the dyes as they are found in the structure of the autochrome, without the overlaid gelatin-silver image layer. The samples in the second set consisted of dyed Whatman filter paper, a group designed to isolate the behavior of the colorants. The third group was composed of samples of the varnish layers on a glass support, allowing observation of the changes occurring in these materials alone. The final group was made up of historical plates. Spectrophotometric measurements were taken of all the samples.

An anoxia protocol was designed specifically for this project. The setup involved assembling the samples on aluminum strips, overlaid by photographic grayscales. The addition of this grayscale allowed the gradational fading rate of the dyes to be measured after light exposure. For each sample, one area was left fully exposed to light, and another fully protected from light using aluminum tape. The aluminum strips with the samples were placed inside custom-made Pyrex glass tubes, closed on each end by threaded plastic caps.

Initially, plastic caps with a rubber O-ring were used that did not provide an impermeable seal. Several attempts to use these were made that included modifications such as lining the glass thread with Teflon™ tape, or covering the gap between the glass and the cap with pressed aluminum foil. The final design used similar plastic caps that were fully lined with a thick layer of Polytetrafluoroethylene (PTFE) for a successful seal. The anoxia tubes were filled with Argon gas humidified to 45%. RP K oxygen scavengers from Mitsubishi Gas Chemical were placed inside each tube to absorb residual oxygen after sealing and Ageless Eye indicators (also from Mitsubishi GC) were included in each tube to monitor the oxygen content. These detect oxygen levels above 0.1%.

The tubes were then transported to the Image Permanence Institute in Rochester, New York, where they were placed in a light-fading unit for 54 days, generously made available to us for this project. The total light received by the samples was 8.29 Megalux-hours, the equivalent to displaying an autochrome on a light box emitting 2,000 lux for nine hours a day over a period of seven months, approximating the average time span of a two-venue museum exhibition.

3. RESULTS AND DISCUSSION

After light exposure, the samples were removed from the tubes and color monitoring was repeated. Erythrosine B, which is red in appearance, and Tartrazine, which is yellow-orange, showed little change under oxygen or low-oxygen light fading. The remaining samples exposed in normal environment conditions containing 21% of oxygen, changed noticeably compared with the samples exposed in a low-oxygen environment. The glass-supported samples show a lower

degree of change in comparison with the paper samples, suggesting there is a protective role played by the overlaying varnish layer as well as the glass supports.

3.1. Light-exposure results on paper and glass supported dye samples

To quantify the degree of change, average color differences or delta E calculations were made. There is a clear reduction of the values of change for the samples exposed under anoxic conditions. However, a complete arresting of the fading was not observed.

Setoglaucine was the dye that presented the most change under low oxygen conditions, both in paper and glass-supported samples. This dye is present in the blue-violet starch filter and this degree of change is consistent with Bertrand Lavédrine's tests that show this as being the most light-sensitive filter in the color screen.

Dye	Sample	Air	Argon
Erythrosine B	Glass	36.4	9.9
	Paper	16.4	0.7
Rose Bengal	Glass	33.8	6.7
	Paper	70.1	6.2
Tartrazine	Glass	0.9	0.8
	Paper	5.2	4.7
Setoglaucine	Glass	14.1	12.7
	Paper	46.9	36.3
Patent Blue	Glass	8.6	4.6
	Paper	37.7	14.1
Crystal Violet	Glass	22.7	6.9
	Paper	81.5	13.0

*Table 1: ΔE CIE L*a*b* Values for sample areas exposed to 8.29 Mlux·hour*

3.2. Light-fading results on varnish samples

In the case of the varnish samples, the calculations for the area of full light exposure show a Delta E above 1 in oxygen, the value above which change that is discernible with the naked eye in the form of a slight yellowing; and of below 1 for the argon conditions. Inspection under long wave ultra-violet revealed a cloudy appearance on the fully exposed area of both oxygen and anoxia samples, but the degree of change observed in the sample exposed to light in normal environmental oxygen levels is much greater than that of the sample exposed under anoxic conditions.

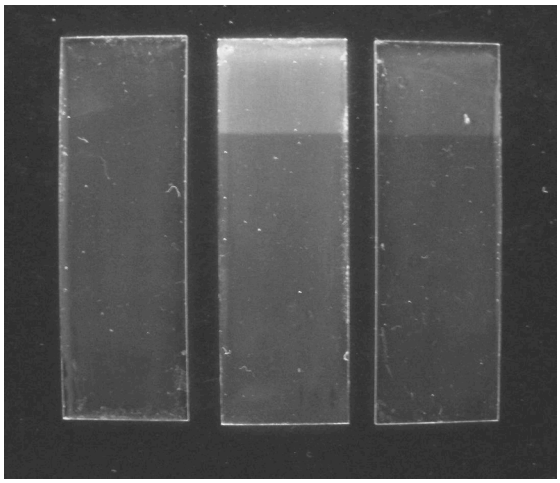

Figure 1: Varnish samples after light-aging under long wave UV. Left: control; center: air; right: low-oxygen.

This increase in fluorescence, as well as the yellowing of the varnish, is a result of autoxidative degradation previously studied and described by René de la Rie for varnish layers on paintings (De la Rie 1982). De La Rie noted, however, that although the degradation of dammar, which is present in both varnishes of these samples, involves photo-chemically initiated autoxidation reactions, these are followed by

non-oxidative thermal processes should exposure to light continue. In this case, anoxic conditions would not be relevant.

Observation under the microscope shows that, when compared with the control samples, both types of exposed varnish samples present a finer cracking pattern after light exposure, a change that is equivalent between the anoxic and the oxygen environment. When looking at the transmission spectra of the varnish samples we can observe that those exposed under anoxic environment did not change significantly from the control, while the samples exposed under normal oxygen environment showed a noticeable decrease of light transmission below around 450 nm towards the ultraviolet region. This same phenomenon was observed in the glass-supported samples that showed a decrease of light transmission in this region. We can attribute these changes to the effect on varnish layer rather than a change in the dye.

3.3. Light-fading results on historical samples

In the historical samples subjected to the first fading test, the general trend observable in anoxia is a shift towards red, while in the oxygen samples the change is towards yellow/green. This is consistent with the rates of fading observed in the individual dye test. In this sample group the degree of change is reduced under anoxic conditions. Under UV illumination there was no difference between the anoxia and oxygen samples, confirming René de la Rie's statement that after the initial oxidative degradation reactions, subsequent deterioration is independent from oxygen (De la Rie 1982).

3.4. Observation of change in density scales

An interesting phenomenon was observed after the fading test. The photographic density scales placed over the samples exposed under environmental oxygen conditions developed intense silver mirroring that was not observed in the samples exposed under anoxic conditions (figure 2). This is unexpected since the most extensive research on this topic by Giovanna Di Pietro (Di Pietro 2002), seemed to point to high humidity and high temperature as the main factors of this form of deterioration, independent from light exposure or presence of oxygen. In the present research the temperature and RH conditions were stable at 25 degrees Celsius and 45% RH. Contact with Di Pietro opened more possible avenues of research. However, this falls outside the main scope of the project, and no further inquiries were made.

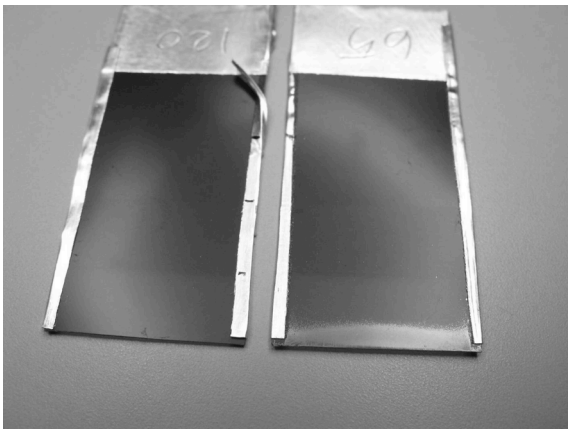

Figure 2: Density grayscales after light-aging experiment. Left: exposed in low-oxygen; right: exposed in air.

4. SECOND LIGHT-FADING EXPERIMENT

The results of the first phase of tests suggested that there could be benefits for these dyes from using anoxic conditions during display. The limited exhibition of original autochrome plates could therefore be possible under controlled conditions. A second light fading test of the dyes in

their red-orange, green and blue-violet combinations was carried out in 2009-2010 using the same methodology of the first test. These results will be published in ICOM-CC's 16th Triennial Conference preprints in September 2011.

5. ANOXIC SEALED PACKAGE

The possibility of exhibiting autochromes meant that an anoxic sealed package had to be designed and exhibition light sources researched. Primary goals for the package were: a passive system, straightforward in application, and economically viable. The initial enclosure design was modeled on the one used by Ralph Wiegandt for daguerreotypes. This utilizes a silicone gasket held under pressure. For our purposes we modified the package to have glass on the front and back for transmitted-light viewing of the object, and added scavengers within the enclosure to absorb any residual oxygen.

A fragment of a historical plate and three red-orange, green and blue-violet samples were bound together, and matted. The mat verso had a cutout to insert oxygen scavengers and an indicator. Aluminum foil was applied to the edges of the mat to protect it from the silicone grease used on the package. The mat was placed between two glasses with a silicone gasket. The gasket was cast with platinum-catalyzed silicone P-4 from Silicones, Inc. (www.silicones-inc.com) that passed the Photographic Activity Test, the Oddy test, and AD strip acid detection in tests carried out by Ralph Wiegandt at George Eastman House (Wiegandt, personal communication). To improve the contact of the gasket with the glass, silicone vacuum grease was applied along the edge. The thickness of the gasket was slightly deeper than that of the matted object. The package was assembled inside a glove bag that had been purged with argon gas humidified to 45%. Metal binder clips maintained an even pressure on the gasket and the glazing, providing the seal. Unfortunately, the glass on this package completely shattered after three days, possibly due to physical expansion of the scavengers. Modifications to this package were tested. An improved design is described in the accompanying article (Casella, Sanderson, 2011).

6. EXHIBITION LIGHTING

Acceptable light sources for possible exhibition of autochromes should emit no UV, no heat, and provide good white balance. Initially it was thought that low energy emission would also be required. This, however, proved not to allow for optimal rendering of the autochrome image.

New light sources recently on the market in 2009 appeared to have great potential in complying with these prerequisites. LEC or Light Emitting Capacitor flat panels emit low energy, no UV and no heat. A unit by the company E-Lite was tested. LEC panels used to be bluish/green but this has been corrected by adding reddish colorants to the panel, and the light output has a more neutral tone. The panel proved not to be bright enough for rendering the details of the autochrome.

LED or Light Emitting Diodes are small light bulbs which produce a very bright light. An LED light panel by Rosco was tested. The color tone and output was very satisfactory but it was found to generate excessive heat, reaching temperatures around 30 degrees Celsius or 86 Fahrenheit after a six hours, measured with a mercury thermometer in direct contact with the panel. The output of energy necessary for a good rendering of the image was 2,000 footcandles in direct contact with the panel. This value reduced to 200 footcandles if the autochrome plate was at a

distance of three feet from the light source. A possible design for a workable display case might place the light source at sufficient distance from the object and include a cooling system or incorporate good ventilation.

OLEDs or Organic LEDs have just started to appear in the market and appear to have promising potential but were not available for testing in North America in 2009.

7. CONCLUSIONS

Although it is clear that keeping autochromes protected from light and at cold temperatures will preserve them indefinitely, this experiment has confirmed that low-oxygen environments reduce the fading rate of the dyes present in the color screen. Although low-oxygen does not eliminate fading, it significantly reduces it within a limited amount of light exposure, making exhibition under controlled conditions a viable option. The dye Setoglaucine appears to develop overall yellowing at all levels of light exposure. A second experiment was concluded in 2010 to establish the exact levels of light after which there is noticeable change for the autochrome dyes in their red-orange, green and blue-violet combination the results of which will be presented and published at the 16th ICOM-CC Triennial Conference in Lisbon, Portugal.

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REFERENCES

- ARNEY, J. S., A. J. Jacobs and R. Newman. 1979. The Influence of Oxygen on the Fading of Organic Colorants. *Journal of the American Institute for Conservation* 18: 108–117.
- BELTRAN, V., J. DRUZIK, and S. MAEKAWA. 2008. An Extended Investigation of the Influence of Oxygen on Color Fading. Poster presented at the *ICOM-CC 15th Triennial Conference, New Delhi, 22-26 September 2008*. Paris: ICOM.
- CASELLA, L. 2009. Autochrome Research at the Metropolitan Museum of Art: Testing Methodology and Preliminary Results for Anoxia Light-Fading. *Topics in Photographic Preservation* 13, comp. B. Bernier and C. Moore, 128-136. Washington D.C.: AIC.
- CASELLA, L., K. Sanderson. 2011. Display of Alfred Stieglitz and Edward Steichen Autochrome Plates: Anoxic Sealed Package and Lighting Conditions. *Topics in Photographic Preservation* 14, comp. B. Bernier and C. Moore. Washington D.C.: AIC.

- DE LA RIE, R. 1982. Fluorescence of Paint and Varnish Layers (Part I). *Studies in Conservation* 27(1): 1-7.
- DE LA RIE, R. 1982. Fluorescence of Paint and Varnish Layers (Part II). *Studies in Conservation* 27(2): 65-69.
- DE LA RIE, R. 1982. Fluorescence of Paint and Varnish Layers (Part III). *Studies in Conservation* 27(3): 1-7.
- DIPIETRO, G. 2002. *Silver Mirroring on Silver Gelatin Glass Negatives.* Inaugural dissertation zur Erlangung des Würde eines Doktor der Philosophie vorgelegt der Philosophisch-Naturwissenschaftlichen Fakultät der Universität Basel. Basel, Switzerland. Available at: http://iaq.dk/silvermirror/index.html (accessed July 2011).
- KRAUSE, P. 1985. Preservation of Autochrome Plates in the Collection of the National Geographic Society. *Journal of Imaging Science* 29 (5): 102–108.
- LAVÉDRINE, B., J.P. GANDOLFO and J.M. SUBSIELLES. 1993. La plaque Autochrome : Analyses Physiques et Chimiques, Étude de la Stabilité des Colorants. In *ICOM-CC 10th Triennial Meeting Preprints, Washington, D.C.*. 1:275–280. Paris: ICOM.
- LAVÉDRINE, B. 2009. *L'Autochrome Lumière. Secrets d'Atelier et Défis Industriels*. Paris: Editions CTHS.
- ROWE, S. 2004. The Effect of Insect Fumigation by Anoxia on Textiles Dyed with Prussian Blue. *Studies in Conservation* 49(4): 259-270.
- TOWNSEND, J., S. HACKNEY, J. THOMAS and A. LERWILL. 2008. The Benefits and Risks of Anoxic Display for Colorants. *Conservation and Access*, ed. D. Saunders, J. H. Townsend and S. Woodcock, 76–81. London: IIC.
- WAGNER, S., C. MCCABE and B. LEMMEN. 2001. Guidelines for Exhibition Light Levels for Photographic Materials. *Topic in Photographic Preservation* 9, comp. S. Wagner, 127-128. Washington D.C.: AIC.

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Papers presented in *Topics in Photographic Preservation, Volume Fourteen* have not undergone a formal process of peer review.

AUTOCHROME RESEARCH AT THE METROPOLITAN MUSEUM OF ART: TESTING METHDOLOGY AND PRELIMINARY RESULTS FOR ANOXIA LIGHT-FADING

LUISA CASELLA

Presented at the 2009 PMG Winter Meeting in Tucson, Arizona

ABSTRACT – The Metropolitan Museum of Art has in its collections an important group of Autochrome plates that have been surveyed and documented in digital image-based condition reports using *Adobe Acrobat*©. It is this collection that provided the context for an investigation of the effectiveness of anoxic environments in delaying the fading of dyes used in the Autochrome process – Tartrazine, Erythrosine B, Rose Bengal, Patent Blue, Crystal Violet, and Malachite Green Orthochlorinated. The dyes were subjected to accelerated light fading in both an atmospheric and an anoxic environment (argon gas with oxygen scavengers). Significant increases in color stability were observed under anoxic conditions, though fading was not completely arrested. A preliminary microfading test was also explored. The sensitivity of Autochrome dyes to light was confirmed: exposure for approximately 8 Mlux-hrs in a standard oxygen environment resulted in visual changes perceptible to an average viewer.

1. INTRODUCTION

The Autochrome was the first commercially viable color photographic process. Introduced by the Lumière brothers in 1907, it remained in production until 1935. The Autochrome was a reversal process that produced one unique image – a positive transparency on a glass support, meant to be viewed by projection or against a light source.

Because of the risk of fading of the color screen layer, the majority of museums and collections now have a policy of not displaying original Autochromes. However, the literature on dye stability has suggested that oxygen is often a critical element in the fading reaction (Arney et al. 1979). This investigation therefore set out to explore the application of anoxic environments to the display of Autochromes.

1.1. THE AUTOCHROME PROCESS

In the Autochrome process, a glass support was covered with a layer of varnish composed of dammar resin and natural rubber dissolved in toluene. This varnish layer remained sticky, adhering the color screen layer, composed of evenly mixed potato starch grains individually dyed orange-red, green and violet-blue. Fine black carbon powder was used to fill remaining gaps between the grains and the layers were then pressed flat in a rolling press. A second varnish composed of nitrocellulose, castor oil, and dammar resin was applied to protect the starch grains from moisture, followed by a panchromatic silver gelatin emulsion,

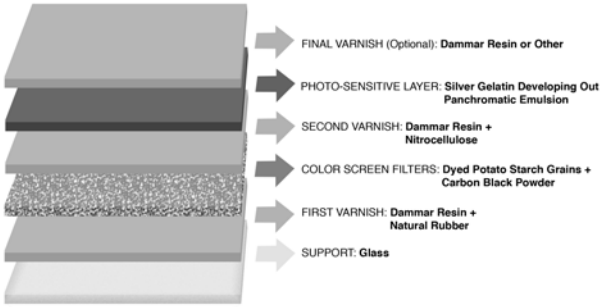


Fig.1. *Autochrome layered structure*

which constituted the light sensitive layer. After exposure in a camera and processing, photographers often coated the image with a further layer of varnish - commonly dammar resin, although other varnishes were also applied (cf. Passafiume 2005).

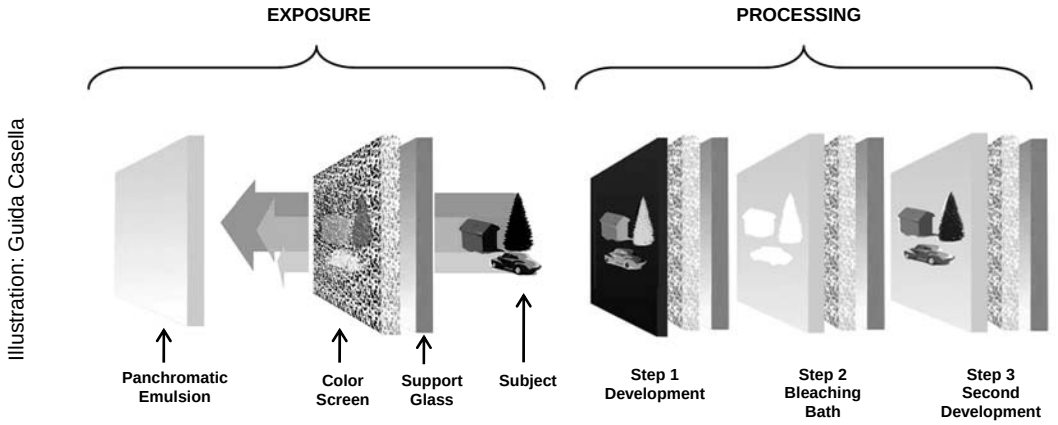


Fig.2. *Exposure and processing steps*

The Autochrome plate was exposed in the camera with the color screen layer facing the subject (fig.2). Light reflected from this subject therefore reached the photo-sensitive silver gelatin emulsion only after passing through the red, green and blue potato-starch filters. Thus, for example, red colored light reflected from the subject would preferentially pass through the red grains affecting the sensitive emulsion in that area, but would be blocked by the green or blue grains.

During the first development, the areas affected by light were reduced to dark metallic silver, resulting in a black and white negative image. At this point, the remaining photo-sensitive silver halides – which had not been affected by light – were still present in the silver gelatin layer. A bleaching solution then removed the black, developed metallic silver, leaving only the still photosensitive silver halides that had not been exposed initially. Next, the plate was exposed to light, affecting the remaining silver salts, and developed a second time. When the resulting black and white positive transparency was viewed in transmitted light, the minute color filters embedded in the color screen produced the effect of a positive image with natural color.[1] Finally, the plates were commonly bound against a cover glass, using a paper tape with a heat activated adhesive.

2. AUTOCHROME COLLECTION AT THE METROPOLITAN MUSEUM OF ART

The Department of Photographs of The Metropolitan Museum of Art in New York has in its collections forty Autochrome plates, primarily by early twentieth-century Pictorialist photographers. Alfred Stieglitz and Edward Steichen, two key figures in the Pictorialist movement, had been present when the Autochrome process was made public by the Lumière brothers in Paris. They then played a pivotal role in the introduction of the process in the United States. The Autochrome process was, however, used by Stieglitz and Steichen's circle for only a short time in the years following 1907 (Hammond 1994) and this has enhanced the rarity and importance of the images in the Metropolitan Museum's collection. The Museum has, in addition, two plates in the Department of Arts of Africa, Oceania and the Americas by Fred Payne Clatworthy and Franklin Price Knott - two photographers known for their contributions to *The National Geographic Magazine* - and a

[1] Because the color screen faces the subject during exposure, to observe an Autochrome in the correct orientation, the silver image layer should face the observer.

group of fifty plates belonging to the Egyptian Department, taken by Harry Burton to document a Metropolitan Museum of Art archaeological expedition to Egypt in the 1920s.

2.1. SURVEY OF THE MET AUTOCHROME COLLECTION

The plates belonging to the Department of Photographs have been surveyed and photographed and individual digital condition reports have been created using *Adobe Acrobat*©. Documenting the condition of objects represents a vital aspect of any conservator's responsibilities. The importance such documentation cannot be overstated, in recording the condition of objects and enabling any changes to be monitored over time. Condition reports are most commonly entered on the Museum's database, *The Museum System*© (TMS).[2] The conservation form has several fields, though condition reports are, for the most part, entered as free text in the 'Remarks' field. Since the location of any damage is difficult to describe accurately in a text format, condition reports are frequently accompanied by a hand-annotated hardcopy of the image.

More recently, *Adobe Acrobat Standard 8*© has been used to generate digital condition reports including images annotated with commenting tools. High quality digital images were taken for these reports by the Museum's Photography Studio, saved in PDF format, and combined, using *Adobe Acrobat*©, in a single document containing multiple views and details of the object. This method offers several advantages: files can be opened using free software (*Adobe Reader*©); documents can include multiple views of the object; digital condition reports can be attached to TMS, e-mailed or printed; and the same document can be used for condition reporting over time. The report is saved on a shared drive that is regularly backed up. In addition, a copy that has no interactive features is saved and linked to TMS. This second copy is electronically more stable in the long-term and has a lower file size than the original report.

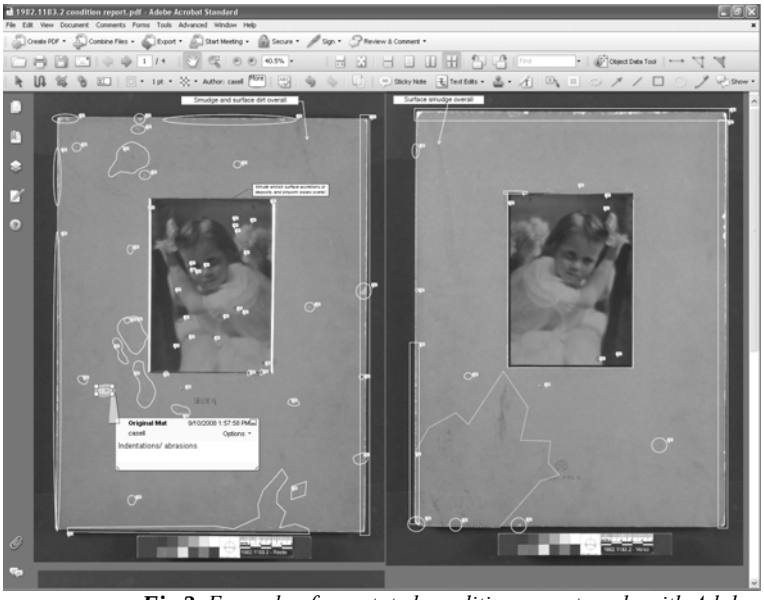


Fig.3. *Example of annotated condition report made with Adobe Acrobat© (seen here plate MMA#1982.1183.2)*

3. ANOXIA EXPERIMENT

3.1. PAST ANOXIA RESEARCH AND RATIONALE

Autochrome plates are generally considered *"extraordinarily light-sensitive"* (Wagner et al. 2001), so facsimiles are usually put on display in place of originals. Past research (Krause 1985; Lavédrine and Gandolfo 1993) has demonstrated that Autochrome plates are very sensitive to moisture and heat as well as light. Light will cause the dyes in the color screen layer to fade; moisture may cause the dyes to dissolve or migrate; heat will cause cracking in the image layer.

[2] *The Museum System*© is a commercial database developed by Gallery Systems, used by many museums in the USA and abroad.

It has been known since the end of the 19th Century that some colorants will be more stable in light if kept in oxygen-free conditions. In 1888, the Russell and Abney Report cited light fastness test results for a variety of watercolor materials, demonstrating that, in the absence of oxygen, the majority of colorants tested were seen to fade at a much slower rate or not at all. Since the Russell and Abney Report, several studies of the effects of anoxia have established that different dyes react differently, so that they have to be tested individually. For example, Prussian Blue, which is found in cyanotypes, will be adversely affected by the absence of oxygen, suffering a photo-reduction reaction and therefore fading.

Anoxic enclosures have been successfully used for the preservation of other museum objects (Maekawa 1998). Research into the application of anoxia to artists' color materials is currently being carried out by the Getty Conservation Institute and Tate Britain (Beltran et al. 2008; Townsend et al. 2008). Yet, the application of anoxic environments to the display of photographic materials has been limited to a few objects of great value, such as Niépce's *Vue de Gras* at the Harry Ransom Center in Austin, Texas, and *The Cincinnati Panorama* daguerreotypes from the Public Library of Cincinnati and Hamilton County, Ohio, for which an anoxic frame was designed by Ralph Wiegandt of George Eastman House in Rochester, New York.

Prior to the present project, research on the application of anoxic environments to color photographic materials, such as Autochromes, had not been undertaken. There is thus no literature on the anoxic light fading behavior of such materials, and specifically of the six dyes present in the Autochrome color screen (table 1).

Table 1: *Dyes in the Autochrome color screen*

Filter	***Dye***	***C.I. Number***	***Other Names***
Orange-red	*Erythrosine B*	*45430*	*Acid Red 51*
	Rose Bengal	*45440*	*Acid Red 94*
	Tartrazine	*19140*	*Acid Yellow 23*
Green	*Patent Blue*	*42051*	*Acid Blue 3*
	Tartrazine	*19140*	*Acid Yellow 23*
Violet-blue	*Crystal Violet*	*42555*	*Basic Violet 3*
	Malachite Green Orthochlorinated	*42025*	*Basic Blue 1*

3.2. EXPERIMENTAL

The experiment was designed with input from and the collaboration of colleagues and experts in the field. Samples were prepared following the historic dilution percentages of the dyes and varnish recipes. Because the purpose of the test was solely to study the color screen, the samples did not have a photosensitive layer. The experimental anoxia setup drew from past research methodologies but called for the development of an original protocol, using custom-made glass tubes sealed with caps. In order to achieve an anoxic environment, the tubes were first purged with argon gas. RP-K System™ scavengers were used to absorb any residual oxygen and monitoring of oxygen concentration was done with Ageless Eye™ oxygen indicators.[3]

Four groups of samples were prepared (see table 2). The first group consisted of dyed potato starch grains[4] on a glass support[5] encased between two varnish layers. The purpose of this group was to

[3] RP-K System™ oxygen scavengers do not affect the relative humidity levels within the sealed environment. These and the oxygen indicators were generously provided by Mitsubishi Gas Chemical America.
[4] Each dye was tested individually rather than in the mixtures found in the Autochrome color screen to form the red, green and blue grains (see table 1).
[5] 1mm thick microscope glass slides were used as support.

observe the behavior of individual dyes as they are found in the structure of the Autochrome plate. The layering order for this batch of samples was as follows: glass/ first varnish/ dyed starch/ second varnish. The second group was created by infusing the colorants into separate pieces of Whatman filter paper.[6] This group allowed the behavior of the dyes to be observed in isolation. The third group was created by applying two varnish layers to a glass support, to show changes such as discoloration or cracking. The layering structure here was: glass/ first varnish/ second varnish. The fourth sample group consisted of historical Autochrome plates. The use of historical samples in accelerated tests can be problematic since their processing and storage history is not known. In this experiment, the behavior of the historical samples served as a comparison with the results in the other groups, giving a measure of what might be expected with actual Autochrome examples.

For each of the four groups, ten duplicates were created, five of which were tested under anoxic conditions and five in a normal atmospheric environment, yielding a total of 140 samples.

Table 2: *Groups of samples produced for the test*

Group 1 *(60 samples)*	*Starch grains dyed with each of the 6 dyes, between varnish layers, on a glass support*
Group 2 *(60 samples)*	*Whatman filter paper saturated with each of the 6 dyes*
Group 3 *(10 samples)*	*The two types of varnish layers on a glass support*
Group 4 *(10 samples)*	*Historical samples*

All the varnish layers on the samples were applied using a spreader to ensure a consistent thickness (fig.4).

The dyed potato starch grains in the first group were applied to the sticky varnish with a soft brush.

The paper samples were prepared by blotting them with cotton saturated with the dye.

Historical samples were purchased at flea markets and cut into small samples for testing.

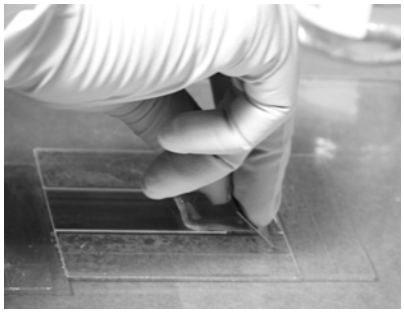


Fig.4. *Applying varnish layer using a spreader*

3.2.1. COLOR AND DENSITY MONITORING

Prior to the fading test, benchmark readings were taken from the paper samples using an X-Rite 968 spectrophotometer. In the glass-supported samples, spectral data was collected using a Cary 50 UV-Vis Spectrophotometer. Polyester sheet overlays were used to ensure consistency of the measurement areas before and after exposure in the light-fading unit.

3.2.2. TESTING SETUP

The samples (nine per tube) were assembled on aluminum strips, overlaid by five-step density grayscales to create a gradational fading rate for the dyes (fig.5). In each sample, one area was left fully exposed, while another was fully protected from light using aluminum tape.

Sample placement was made in a random manner in each tube, so that, in the event that one or more of the tubes

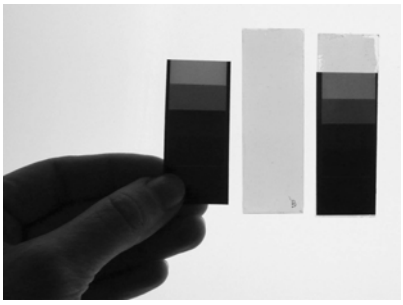


Fig.5. *Grayscales were placed over the samples*

[6] Whatman Qualitative Filter Paper No.1.

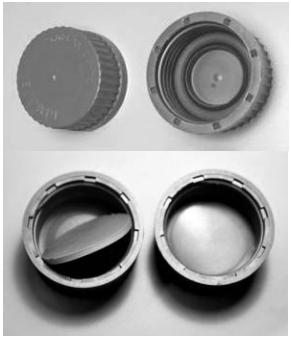
should experience oxygen ingress, part of the data could still be retrieved.

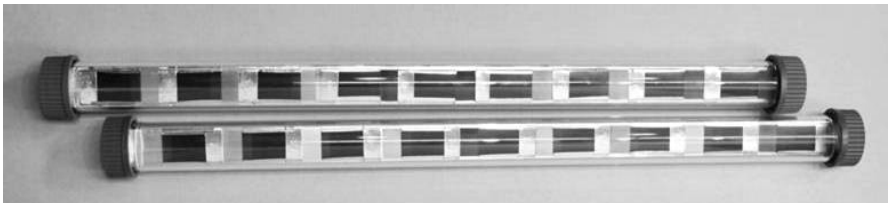
The aluminum strips were placed inside custom-made, low expansion borosilicate glass tubes[7] sealed on each end with plastic caps. The decision not to use heat-sealed glass ampoules, which would have been very efficient (Arney and Jacobs 1979), arose from the desire to create a practical and reusable experimental set-up that could be easily sealed, without requiring the services of a glass technician.

Achieving a successfully sealed oxygen-free environment inside the tubes involved several failed attempts - failure being caused by the permeability of the caps used initially. For the final setup, the caps used had a thick PTFE[8] lining (fig.6.).

The eight anoxia tubes were filled with Argon gas humidified to 45% RH. The moisture content of the argon was adjusted before introducing it into the tubes by mixing the dry gas directly from a cylinder with moist gas which passed through a water trap filled with distilled water. The purging process of each tube was constantly monitored using an oxygen analyzer (Illinois Instrument, Inc. Model 911) and oxygen concentration was lowered to less than 500ppm. Three RP-3K System™ oxygen scavenger pouches were placed inside each tube to absorb any residual oxygen[9], together with one Mitsubishi Ageless Eye™ oxygen indicator to monitor oxygen concentration during light exposure.

Top: plastic caps with O-rings (O_2 setup). Bottom: PTFE lined plastic caps (Argon setup)





Anoxia tubes include RP™ System O_2 Scavengers and Ageless Eye™ O_2 Indicators (top: recto; bottom: verso)

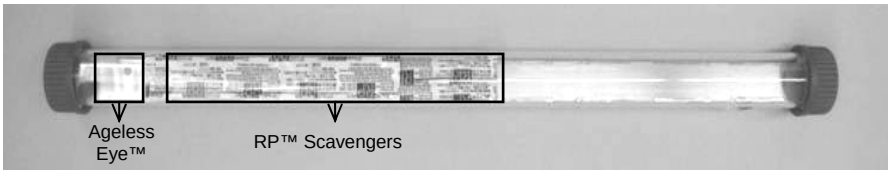


Fig.6. *Testing Setup*

And additional eight tubes, identical in every way except that they contained normal atmospheric oxygen levels and did not include oxygen scavengers, were sealed in a 45% RH environment.

A third set of samples was kept in the dark, inside an aluminum foil pouch, under ambient conditions, as a control.

3.3. ACCELERATED FADING

The tubes were wrapped in aluminum polyethylene foil to protect them from light and transported to the Image Permanence Institute at Rochester Institute of Technology, where they were placed for 54 days in a light fading unit with fluorescent lamps with very low UV content, emitting 6400lux[10], for a total of 8.29Mlux-hours. This would be the equivalent to displaying an Autochrome on a

[7] The tubes were manufactured by Kimble-Kontes using Corning Pyrex 7740, which has a refraction index of 1.474.
[8] Polytetrafluoroethylene.
[9] RP-K System™ oxygen scavengers are available in two levels of oxygen absorption: 300cc (RP-3K) and 500cc (RP-5K). Tak Izawa from Mitsubishi Gas Chemical America calculated that 3 pouches of RP-3K in each tube would provide an excess of scavenger to absorb residual oxygen for the volume of the tubes.
[10] Twelve cool fluorescent lamps (Sylvania F40/CWX).

common light box emitting 2000lux for 9 hours a day over a period of 20.95 months. An exhibition period of about 3 months would represent an exposure of 2Mlux-hours - one quarter of the total light fading test exposure.[11]

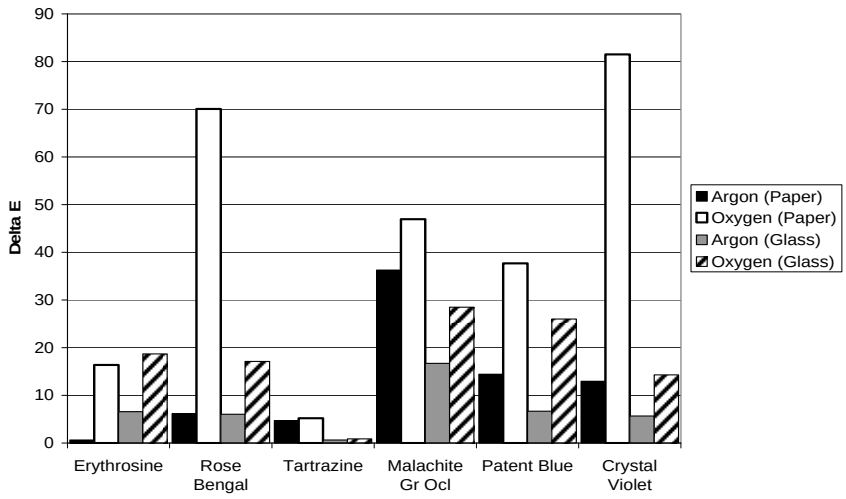
In the light fading unit, the lamps moved while the samples stayed in place to ensure the homogeneity of the light exposure of all the samples. Constant ventilation prevented heat build-up and maintained a temperature of 25°C, measured using a Raytek Raynger ST™ non-contact thermometer on the surface of the glass tubes.

3.4. RESULTS

After exposure in the light fading unit, the experiment tubes were wrapped in aluminum polyethylene foil and transported back to The Metropolitan Museum of Art. The samples were removed from the tubes as promptly as possible. Densitometry and spectrophotometry readings were made of each sample, measuring the five areas of graded exposure and the one control, giving a total of six measurements from each sample.

Graph 1 illustrates the ΔE[12] values recorded by the samples from groups 1 and 2 (see table 2), in the area of the sample that was fully exposed to light. The results show the clear benefit to all the dyes, to a greater or lesser degree, from the anoxic environment. Clear instances of this are the Crystal Violet and Rose Bengal, which show a considerable decrease in fading under anoxic conditions. Malachite Green Orthochlorinated is the dye showing the least benefit from anoxia. Tartrazine is the most stable dye and shows very little fading in any environment.

A full account of the data resulting from the test will be included in a future article.



Graph 1: *Relative stability of glass and paper samples based on ΔE76*

4. MICROFADING EXPERIMENT

The microfader is an analytical tool that collects light fading data on a minute testing area (100µ in diameter). The assessment of lightfastness is done at a very early stage of fading that is not discernable by the human eye but is measurable by the spectrophotometer. The microfader combines in its probe a single optical fiber cable that focuses an intense light on the area to test, and a spectrophotometer that measures the resulting change.

[11] Although in actual exhibition conditions, original Autochromes would not be constantly illuminated but would more likely be displayed using a motion or visitor activated light box.
[12] The equation used was ΔE 76 following what was used in most of the references.

In collaboration with Chris McGlinchey at the Museum of Modern Art in New York, accelerated aging studies were conducted on test samples of dyed Whatman filter paper using a microfader unit fitted with a close contact bifurcated fiber optic head designed to purge oxygen from the sample area during the test. Were this method to prove a viable means of carrying out tests in anoxia, it would then be possible to assess the benefits of anoxic exhibition without having to create a chamber for the entire object, making it much more convenient and economical to evaluate individual objects. Preliminary results are promising and will be the subject of a future publication.

5. CONCLUSIONS

Developing the methodology for anoxic testing was challenging. The choice of a reusable system of glass tubes with caps provided a successful setup for creating an anoxic environment. The Autochrome dye samples exposed to light in normal environment conditions show a marked color shift due to light exposure. The results of the experiment demonstrate the clear benefit of anoxia in decreasing the fading rate, though the complete arrest of fading was not achieved. The protective role played by the varnish layers is confirmed, as is evident from a comparison between the results from the samples of dyes in paper with those from the dyes on a glass support, which show a significant difference (table 2, groups 1 and 2). The specific results of the test, together with their interpretation, will be published in the near future. By analyzing the gradational fading data, it will be possible to establish precise light level recommendations for Autochrome display under anoxic conditions.

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REFERENCES

Arney, J. S., A. J. Jacobs and R. Newman. 1979. The Influence of Oxygen on the Fading of Organic Colorants. *Journal of the American Institute for Conservation* 18: 108–117.

Beltran, V., J. Druzik, and S. Maekawa. 2008. An Extended Investigation of the Influence of Oxygen on Color Fading. Poster presented at the ICOM-CC 15th Triennial Conference, New Delhi, India.

Hammond, A. 1994. The Autochrome and the Photo-Secession. *History of Photography* 18(2). London – Washington D.C.: Taylor & Francis.

Krause, P. 1985. Preservation of Autochrome Plates in the Collection of the National Geographic Society. *Journal of Imaging Science* 29 (5):182–192.

Lavédrine, B. and J.P. Gandolfo. 1993. La plaque Autochrome : Analyses Physiques et Chimiques, Étude de la Stabilité des Colorants. *ICOM Committee for Conservation preprints.* 10th Triennial Meeting, Washington, D.C.. Paris: ICOM. 1:275–280.

Lavédrine, B. 2009. *L'Autochrome Lumière. Secrets d'Atelier et Défis Industriels*. Paris: Editions CTHS.

Maekawa, S. 1998. *Oxygen-Free Museum Cases*. USA: The J. Paul Getty Trust.

Passafiume, T. 2005. Photography in Natural Colors: Steichen and the Autochrome Process. In *Coatings on Photographs: Materials, Techniques and Conservation*, ed. C. McCabe. Washington, D.C.: American Institute for Conservation of Historic and Artistic Works.

Russell, W.J., and W. de W. Abney. 1888. *Report to the Science and Art Department of the Committee of Council on Education, on the Action of Light on Watercolours*. London: Great Britain Education Department, HMSO.

Townsend, J., S. Hackney, J. Thomas and A. Lerwill. 2008. The Benefits and Risks of Anoxic Display for Colorants. *Conservation and Access*, ed. D. Saunders, J. H. Townsend and S. Woodcock. IIC: London. 76–81.

Wagner, S., C. McCabe and S. Lemmen. 2001. Guidelines for Exhibition Light Levels for Photographic Materials. *Topic in Photographic Conservation* 9. AIC: Washington D.C. 127–128.

Vitale, T. 1998. Light Levels Used in Modern Flatbed Scanners. *RLG DigiNews* 2(5). http://www.worldcat.org/arcviewer/1/OCC/2007/08/08/0000070519/viewer/file3571.html#technical (accessed 8/15/2009)

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Papers presented in *Topics in Photographic Preservation, Volume Thirteen* have not undergone a formal process of peer review.

4. Segunda fase de investigação – testes de envelhecimento acelerado dos corantes presentes nas placas autochrome nas combinações vermelho-laranja, azul-violeta e verde

Apresenta-se em seguida o artigo publicado referente à segunda fase de investigação do projecto:

- "Light-fastness of autochrome color screen filters under anoxic conditions" (2011). Coautoria Masahiko Tsukada e Nora Kennedy. *ICOM-CC 16th Triennial Meeting Preprints*. pp. 1-9.

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LIGHT-FASTNESS OF AUTOCHROME COLOR SCREEN FILTERS UNDER ANOXIC CONDITIONS

Keywords: autochrome, color-screen, anoxia, light-fading, dyes, exhibition

ABSTRACT

The autochrome was the first commercially viable photographic color process. Due to the poor light fastness of the dyes present in the color screen, the majority of cultural institutions have a policy of not displaying original autochrome plates. This project focused on the light fastness, under low oxygen conditions, of the six dyes present in the autochrome color screen in their red-orange, green and blue-violet combinations. Samples produced following the historic formulations were exposed to 8.29 Megalux·hours of light. Spectrophotometric data was collected before and after exposure. For one sample group, a closed setup was designed that created a close to anoxic environment (less than 0.1 percent of oxygen). A comparison group was exposed to light in normal air conditions (about 21 percent of oxygen). Results indicate a benefit of anoxia in slowing the fading rate of the autochrome color screen at high levels of light exposure.

RÉSUMÉ

L'autochrome a été le premier procédé de photographie en couleur viable sur le plan commercial. En raison de la faible solidité à la lumière des colorants présents dans le filtre coloré, la plupart des institutions culturelles ont pour politique de ne pas exposer les autochromes originaux. Ce projet a étudié la solidité à la lumière, dans des conditions de faible teneur en oxygène, des six colorants présents dans le filtre coloré autochrome, dans leurs combinaisons rouge-orange, vert et bleu-violet. Des échantillons produits conformément aux formulations historiques ont subi une exposition à la lumière équivalant à 8,29 mégalux.heure. Les mesures spectrophotométriques ont été recueillies avant et après exposition. Pour un premier groupe

INTRODUCTION

The autochrome was the first commercially viable color photographic process. It was first patented in 1903 by *A. Lumière et Ses Fils,* and marketed from 1907 to 1935. This was a color screen process: a layer containing red-orange, green and blue-violet filters under a silver-gelatin panchromatic emulsion made it possible to separate the colors of the visible spectrum during exposure and, after reversal development, the same filters provided the appearance of a full color image (Figures 1 and 2). The color screen layer was composed of a first varnish made with natural rubber, that remained sticky; potato starch grains dyed red-orange, green, and blue-violet, that constitute the actual color filters; very fine black carbon powder to fill the gaps between the color filters; and a second nitrocellulose and dammar varnish layer to protect the filters from moisture (Lavédrine 2009).

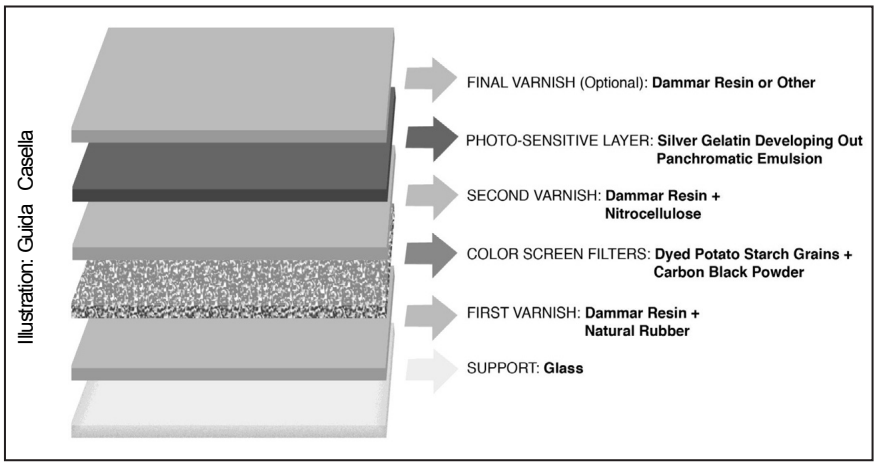

Figure 1
Autochrome structure

The conservation concerns with autochromes include the physical fragility of the glass support and the sensitivity of the various components to temperature, relative humidity and light (Krause 1985). Light in particular is considered greatly damaging to the dyes present in the color screen filters. The poor light fastness of this layer accounts for the majority of cultural institutions having a policy of not displaying original autochrome plates (Wagner et al. 2001).

Anoxia studies applied to artists' color materials demonstrate that the fading mechanism of certain colorants occurs due to photo-oxidation and that if these

d'échantillons, un espace fermé a été conçu en vue de créer un environnement proche de l'anoxie (moins de 0,1 pour cent d'oxygène). Un groupe comparatif a été exposé à la lumière dans des conditions atmosphériques normales (environ 21 pour cent d'oxygène). Les résultats montrent la supériorité de l'anoxie pour ralentir la vitesse de dégradation du filtre coloré de l'autochrome en cas de forte exposition à la lumière.

RESUMEN

La placa autocroma fue el primer procedimiento fotográfico en color disponible a nivel comercial. Debido a la poca fotoestabilidad de los colorantes presentes en la pantalla de color, la mayoría de instituciones culturales tienen como norma no exponer placas autocromas originales. Este proyecto se centró en la fotoestabilidad, en condiciones bajas de oxígeno, de los seis colores presentes en la pantalla autocroma de color, en sus combinaciones rojo-naranja, verde y azul-violeta. Varias muestras reproducidas según las fórmulas antiguas fueron expuestas a una iluminación de 8.29 megalux/hora. Se recolectaron datos espectrofotométricos antes y después de la exposición. Para un grupo de muestras, se diseñó un entorno cerrado que recreaba un ambiente casi anóxico (menos de 0,1% de oxígeno). Un grupo control se expuso a la luz en condiciones normales de aire (alrededor de 21% de oxígeno). Los resultados indican que en condiciones con niveles altos de exposición a la luz, la anoxia reduce la velocidad a la que desaparece el color de la pantalla autocroma.

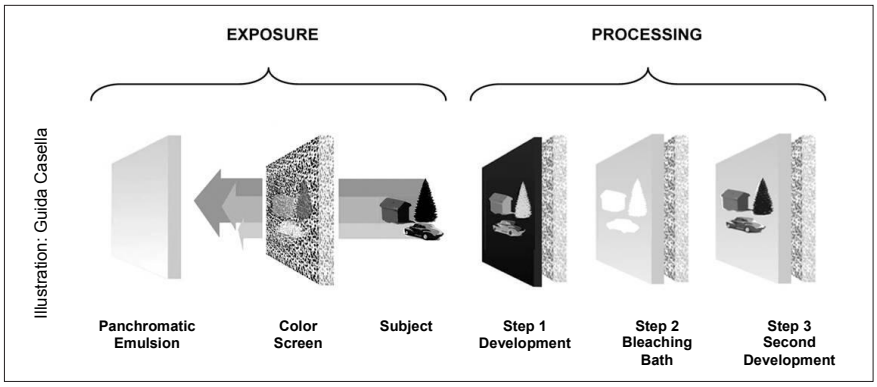

Figure 2
Autochrome exposure and processing steps

are exposed under anoxic conditions they will not fade (Arney 1979, Beltran et al. 2008, Townsend et al. 2008). This is not true of all colorants, however, as is the example of Prussian Blue, which will show change in the absence of oxygen (Rowe 2004), therefore each material has to be tested individually.

Six dyes have been identified in the autochrome color screen layer – Tartrazine, Erythrosine B, Rose Bengal, Flexo Blue, Patent Blue and Crystal Violet (Lavédrine et al. 1993). An additional two dyes were identified that are impurities and therefore were not considered for this experiment: Diiodofluorescein and Malachite Green Meta-Chlorinated. These six dyes were combined to form the red-orange, green, and blue-violet used for the color screen filters (Table 1). They were used consistently throughout the entire period of commercial production of the process (Lavédrine et al. 1993).

Table 1
Dyes present in the autochrome color screen

Filter	Dye	C.I. Number	Other Names	Appearance
Orange-red	Erythrosine B	45430	Acid Red 51	Yellow
	Rose Bengal	45440	Acid Red 94	Magenta
	Tartrazine	19140	Acid Yellow 23	Red
Green	Patent Blue	42051	Acid Blue 3	Blue
	Tartrazine	19140	Acid Yellow 23	Red
Violet-blue	Crystal Violet	42555	Basic Violet 3	Purple
	Flexo Blue	42025	Setoglaucine, Basic Blue 1	Blue

The research at The Metropolitan Museum of Art investigated the potential benefits of using anoxic conditions for the safe display of autochromes. A first phase of this project tested the behavior of the six individual dyes (Casella 2009). The second phase, described in this article, tested the dyes in the historic formulation used to form the three color filters. In addition, a group of historical samples was submitted to the light-fading test.

LIGHT FASTNESS OF RED-ORANGE, GREEN AND BLUE-VIOLET COLOR FILTERS

Test samples were prepared using historic recipes for dye concentrations and varnish compositions (Lavédrine 2009). Test groups for the three

Table 2
Historic formulation of dye solutions to tint the color screen filters

Orange-red filter:	Green filter:	Violet-blue filter:
Distilled water – 100ml	Distilled water – 100ml	Distilled water – 100ml
Erythrosine B – 14.5g	Ammonia – 9g	Crystal Violet – 7g
Rose Bengal – 2.6g	Tartrazine – 21g	Flexo Blue – 1g
Tartrazine – 19.7g	Patent Blue – 10g	
	Sodium Sulfate – 21g	

separate potato starch color filters red-orange, green, and blue-violet were created. For each color filter, one test group was exposed to light under close to anoxic conditions (less than 0.1% oxygen) and a second group under normal air conditions (circa 21% oxygen). Five duplicates were created for each group, for a total of 30 samples.

Sample preparation

The dye solutions were prepared according to the original concentrations in autochrome plates (Table 2). Since the resolution of the image was not critical for the present experiment, a single separation of starch grains by flotation was done to be able to create a layer of dyed starch of fairly homogeneous grain size. The selected starch grains were mixed with the dye solutions following the historical dye to starch ratio: for the red-orange filter 2.3 g of solution were used to dye 3 g of starch; for the green filter, 2.24 g of solution were used to dye 3 g of starch; for the blue-violet filter 2.25 g of solution were used to dye 3 g of starch.

The preparation of the two varnishes was done following the historical recipes. Dammar resin was dissolved in ethyl acetate (9.6 g of resin in 100 ml of solvent). The solution was filtered, separating a white solid residue from the solute. The solid residue was dissolved in toluene in a 10% solution. The first varnish was prepared by dissolving 1.5 g of unvulcanized natural rubber in 87 ml of toluene and adding 5.6 ml of the dammar residue solution. The second varnish was prepared by dissolving 2.4 g of nitrocellulose in the filtered solution of dammar resin in ethyl acetate, and adding 1.5 g (1.44 ml) of castor oil.

Microscope glass slides were used as the sample supports. The first varnish layer was applied with a spreader and left to set. The dyed potato starch grains were applied on this sticky varnish layer with a soft brush in a stippling mode. Finally, the second varnish was applied with a spreader and left to dry. Carbon black was not used to fill gaps between the starch grains as would have been done historically.

Testing setup

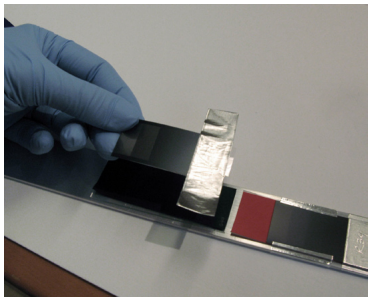

Figure 3
Placing samples on aluminum strips under density step wedges. One area was left fully exposed to light and one area fully protected from light with 3M 425 aluminum tape

The samples were placed on aluminum strips, under custom made photographic step wedges with 5 density areas (Figure 3). One area of the sample was left fully exposed, and one fully covered with 3M 425 aluminum tape. The aluminum strips were placed inside custom made Corning Pyrex 7740 tubes. The threaded ends were closed with plastic caps with a thick PTFE liner. The low oxygen group was purged with argon gas humidified to 45% RH. The purging process of each tube was constantly monitored using an oxygen analyzer (Illinois Instrument, Inc. Model 911) and the oxygen concentration was lowered to less than 500ppm. Inside each tube three RP-K System oxygen scavenger pouches were placed to absorb any residual oxygen, and one Mitsubishi Ageless Eye oxygen indicator to monitor the oxygen concentration during light exposure. The indicators detect oxygen concentrations above 0.1%

(Figure 4). The second group was sealed under atmospheric oxygen conditions at 45% RH.

Light fading conditions

The samples were exposed for 54 days in a fading unit at the Image Permanence Institute in Rochester, NY, with Sylvania F40/CWX fluorescent lamps. The illuminance at the sample surface was 6400 lux, with a total light dose of 8.29 Megalux·hours over the exposure period. The Pyrex 7740 used for the glass tubes transmits more than 90% of visible light. The light exposure period can be considered equivalent to displaying an autochrome in a common light box, emitting 2000 lux for 9 hours a day over a period of approximately 14 months. Refer to Table 3 for the light level values of each exposure area under the density step wedges. The surface temperature of the glass tubes stayed at 25°C as measured with a Raytek Ranger ST non-contact thermometer.

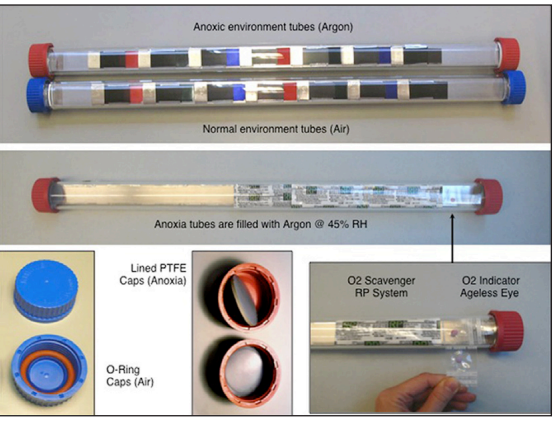

Figure 4
Anoxia setup

Table 3
Calculation of light level equivalent for each exposure step of the experiment

	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6
Optical Density of Step Wedges (Vis)	Fully exposed	0.59	1.03	1.72	1.84	Totally covered
Transmission (%)	100	25.7	9.33	1.91	1.45	0
Light Dose (lx•hrs)	8,290,000	2,130,858	773,668	157,963	119,827	0
Equivalent Days of Exposure in 2000lx, 9hrs per day	460	118	43	9	7	0
Equivalent Days of Exposure in 500lx, 9hrs per day	1842	473	172	35	26	0

Color monitoring

Before and after light fading, transmission spectral data was collected using a Varian Cary 50 Bio UV-Vis spectrophotometer, which is equipped with a Xenon flash lamp as a light source and a 1cm^2 silicon photodiode as a detector. In this study, measurements were performed at 5 nm intervals between 360 and 830 nm, averaging three readings in each area. Polyester sheet overlays were used to ensure consistency of the reading areas.

To quantify the degree of change, the three coordinates of CIE (Comission Internationale de l'Eclairage) L*a*b* of each sample were obtained using the instrument's software with the settings at D50 illuminant with a 2 degree observer. The color difference or Delta E before and after light exposure at the same spot on each sample was calculated according to CIE 1976, which was the standard used in most of the bibliographic references consulted. The resulting Delta E value for each of the five sample duplicates was averaged and is summarized in Table 4. The standard deviation values are at times quite high, denoting a great degree of variation among samples, possibly due to the heterogeneity of the dye application during sample preparation.

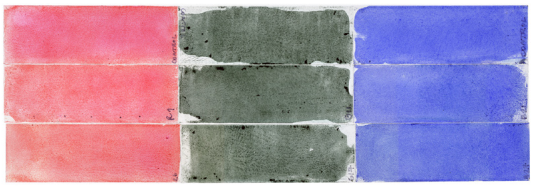

Figure 5
Red-orange (left), green (center) and blue-violet (right) samples after light exposure to 8.29 Mlux·hours. Control group along top, anoxia along center and air group along bottom rows

Table 4
Average Delta E values with D50 illuminant obtained for the dye sample group at the 6 measured areas, from full exposure (area 1) to fully covered (area 6). Refer to Table 3 for corresponding lux·hour values. The values in parenthesis are the standard deviation of averaging the five samples in each group

Delta E (D50 Illuminant)	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6
Red-orange / Air	18.2 (1.9)	14.0 (1.5)	12.0 (1.2)	9.6 (0.9)	9.9 (0.9)	8.8 (1.6)
Red-orange / Anoxia	7.9 (1.6)	6.7 (1.4)	5.5 (0.9)	4.0 (0.6)	4.0 (0.4)	2.6 (2.1)
Green / Air	4.2 (0.6)	2.0 (0.5)	0.8 (0.2)	0.8 (0.9)	0.8 (0.4)	0.5 (0.3)
Green / Anoxia	2.3 (0.2)	1.2 (0.2)	1.0 (0.1)	0.8 (0.2)	0.9 (0.3)	0.8 (0.2)
Blue-violet / Air	27.4 (1.7)	20.0 (2.0)	17.4 (2.3)	11.4 (2.3)	11.4 (0.6)	3.8 (1.4)
Blue-violet / Anoxia	17.9 (2.2)	14.3 (1.3)	13.2 (1.0)	10.2 (1.7)	11.1 (0.9)	4.6 (1.9)

Results and discussion

Considering that the degree after which change is perceivable by the human eye is Delta E 1.5 (just noticeable difference or JND), the results in Table 4 indicate that the vast majority of areas measured in all the samples present perceivable changes. Interestingly, a value higher than JND is recorded in the areas that were fully protected from light (Area 6) in four out of six color screen samples. In one case, the Delta E is as high as 8.8. This occurs with the red-orange samples exposed to light in normal air conditions. In a study on the individual dyes carried out at a first phase of this project, similar results were observed in the areas fully protected from light. This was especially evident in the samples of Erythrosine B and Rose Bengal, both present in the red-orange filter, which showed the first and the second highest change of the sample group in the fully protected areas after light exposure (an article on this first phase has been submitted and is under consideration for publication). It is apparent that factors other than light exposure may have caused this change. Heterogeneity of the samples or temperature may have been responsible. Although the surface temperature of the glass tubes was maintained at 25°C, the temperature inside the tubes could not be measured. Further investigation, including a dark aging experiment, would be necessary to clarify this phenomenon fully.

The degree of change recorded by the spectrophotometer is not easily discernible in the samples by visual inspection (Figure 5) as would be expected with such high Delta E values as shown in Table 4. Figure 6 illustrates how the blue-violet color filter is the least stable to light in both anoxia and air environments, followed by the red-orange and finally the green filter. It is also possible to observe that for all filters there is a decrease of change under anoxic conditions, especially at higher levels of light exposure. The exceptions are the green filter that shows slightly lower degrees of change in air in Areas 3 and 5, and the blue-violet filter in air in Area 6, but these changes are lower than JND or are observed in the unexposed areas (Area 6) where the cause of change is unclear. In spite of the uncertainty of the cause of change in Area

6, comparative results from all other areas generally support the positive influence of a low-oxygen environment on the autochrome dyes.

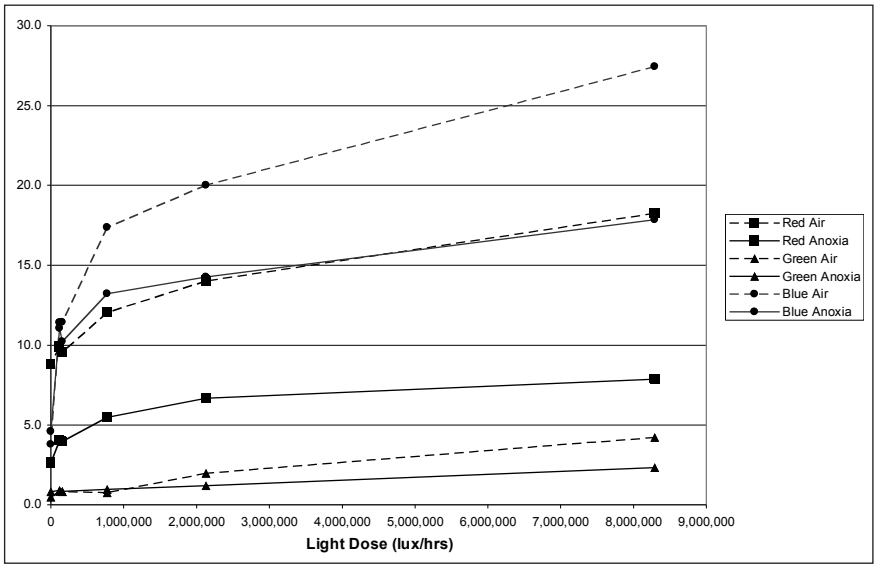

Figure 6
Plot of the Delta E values presented in Table 4

LIGHT FASTNESS OF HISTORICAL SAMPLES

Historical samples in aging tests are often problematic since their storage conditions over time are not known. However, the authors were interested in producing data from historical materials that could be compared to the results of the newly prepared samples.

Sample selection and test conditions

A sample group consisting of historical autochrome plates still in the manufacturer's boxes that had never been exposed or processed was subjected to light fading under the same conditions described above. It was possible to gather samples dating from 1908, 1910, 1912 and 1920, dates inferred from the expiration notices on the original boxes. The use of historic samples that had undergone dark aging, but presumably little light exposure, eliminates one of the variables usually encountered with processed original materials. In order to measure the spectral data of the color screen alone, the layer of silver-gelatin, now milky in appearance, was mechanically removed. The plates were cut to the same size as the experimental samples. Spectrophotometric data was collected before and after the light fading in the same manner as for the fresh dye samples.

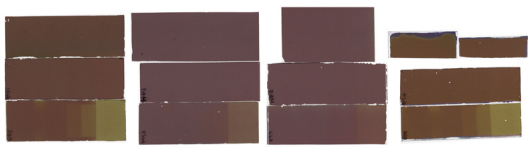

Figure 7
Historical samples after light exposure to 8.29 Mlux·hours. From left, samples dated 1908, 1910, 1912 and 1920. Control group along top, anoxia along center and air group along bottom rows

Results and discussion

Visual inspection of the historical samples plainly illustrates a great difference between those exposed to light under the close to anoxic environment (less than 0.1% oxygen) and those exposed in normal air conditions (Figure 7). It is also evident that, although the dyes used in the production of the color screen were consistent throughout the entire period of production

Table 5
Delta E values obtained for the historical samples group at the 6 measured areas of exposure, from full exposure (area 1) to fully covered (area 6). Refer to Table 3 for corresponding lux·hour values

	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6
1908 Sample (62) Air	22.61	13.05	5.71	2.38	2.34	1.07
1908 Sample (61) Anoxia	1.69	1.31	1.54	0.63	0.63	0.67
1910 Sample (64) Air	10.75	4.93	1.78	0.09	0.73	0.36
1910 Sample (63) Anoxia	1.27	0.31	0.69	0.41	0.76	0.88
1912 Sample (66) Air	6.69	3.9	1.69	1.09	1.51	0.99
1912 Sample (65) Anoxia	0.95	0.01	0.64	1.55	2.03	0.99
1920 Sample (68) Air	22.07	12.65	6.15	2.68	3.1	2.75
1920 Sample (67) Anoxia	1.85	1.39	0.87	2.26	0.8	0.91

(Lavédrine et al. 1993), the exposure to light will have different effects in specific objects, which is possibly related to the storage conditions over time. With these four samples, visual inspection alone indicates the degree of protection provided by the anoxic conditions from light induced damage.

Delta E 1976 values were calculated for all the areas monitored for the test (Table 5). There is a great difference noted between the anoxia and the air exposed samples, the latter group showing a greater degree of change. The results indicate that for historical samples there is a definite benefit from low-oxygen environment in exposure to light, particularly at higher levels of light exposure. Figure 8 illustrates how the samples appear to plateau under anoxia at any level of exposure, whereas under normal air conditions the change recorded continues to increase with greater light exposure.

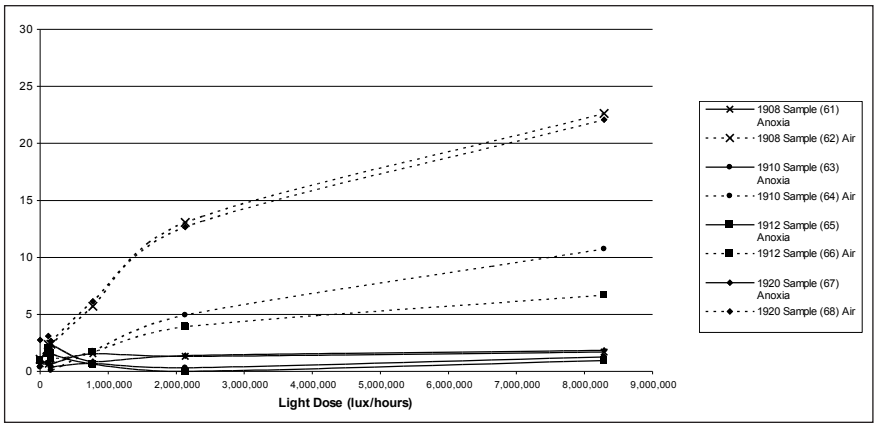

Figure 8
Plot of the Delta E values presented in Table 5

CONCLUSION

The results of the experiment show that the fading rate of all of the autochrome color filters is lower under anoxic conditions. However, the degrees of change are not linear at all levels of light exposure and the areas that were fully protected from light during the test also recorded change after the test, particularly in the newly prepared dye samples. This result should be further investigated to determine if it is related to heterogeneity of the

sampled area and subsequent difficulty in spectrophotometric measurement, or if indeed a change is occurring due to variations in temperature and relative humidity inside the test chamber.

In the historical sample group there was an evident benefit of anoxic conditions with regard to light exposure, suggesting that this may be a safe approach for displaying original autochromes for brief periods of time. Because the color change after light exposure was below JND or almost unperceivable, well-designed anoxic enclosures combined with controlled light types and very brief exhibition times may be a cautious alternative to the current non-display policies in place for these objects. Light levels should only be high enough for viewing. Exhibition times of a maximum of seven days should be combined with viewer-activated illumination to further reduce exposure. As described above, however, until we clearly understand the behavior of the three separate color screens on the areas unexposed to light (Area 6) through further research, extreme caution should be taken with the display methods for autochromes.

There is unique potential of anoxic environments for preserving colorants on display as well as providing a cost effective storage method to reduce oxidative degradation mechanisms. The methodology and results of this experiment contribute information that is applicable to other cultural objects that include these same dyes in their composition.

ACKNOWLEDGEMENTS

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REFERENCES

ARNEY, J. S., A. J. JACOBS and R. NEWMAN. 1979. The influence of oxygen on the fading of organic colorants. *Journal of the American Institute for Conservation* 18: 108–117.

BELTRAN, V., J. DRUZIK, and S. MAEKAWA. 2008. An extended investigation of the influence of oxygen on color fading. In *ICOM-CC 15th Triennial Conference, New Delhi, 22–26 September 2008,* ed. J. Bridgland, 820. New Delhi: Allied Publishers Pvt. Ltd.

CASELLA, L. 2009. Autochrome research at The Metropolitan Museum of Art: testing methodology and preliminary results for anoxia light-fading. *Topics in Photographic Preservation* 13, comp. B. Bernier and C. Moore, 128–136. Washington D.C.: AIC.

KRAUSE, P. 1985. Preservation of autochrome plates in the collection of the National Geographic Society. *Journal of Imaging Science* 29(5): 182–192.

LAVÉDRINE, B., J.P. GANDOLFO, and J.M. SUBSIELLES. 1993. La plaque autochrome: analyses physiques et chimiques, étude de la stabilité des colorants. In *ICOM-CC 10th Triennial Meeting Preprints, Washington, D.C., 22–27 August 1993,* Vol. 1: 275–280. London: James & James.

LAVÉDRINE, B. 2009. *L'Autochrome Lumière. Secrets d'atelier et défis industriels*. Paris: Editions CTHS.

ROWE, S. 2004. The effect of insect fumigation by anoxia on textiles dyed with Prussian Blue. *Studies in Conservation* 49(4): 259–270.

TOWNSEND, J., S. HACKNEY, J. THOMAS, and A. LERWILL. 2008. The benefits and risks of anoxic display for colorants. *Conservation and Access*, ed. D. Saunders, J.H. Townsend and S. Woodcock, 76–81. London: IIC.

WAGNER, S., C. MCCABE, and B. LEMMEN. 2001. Guidelines for exhibition light levels for photographic materials. *Topics in Photographic Preservation* 9, comp. S. Wagner, 127–128. Washington D.C.: AIC.

MATERIALS LIST

Ageless Eye™ oxygen indicators
Supplier: Mitsubishi Gas Chemical America
http://www.mgc-a.com

Aluminum Tape 3M 425
Supplier: Grainger
http://www.grainger.com

Corning Pyrex® 7740 glass tubes
Supplier: Kimble–Kontes
http://www.kimble-kontes.com

Crystal Violet CI 42555 (Basic Violet 3)
Supplier: SIAL/Sigma–Aldrich
http://www.sigmaaldrich.com

Erythrosine B CI 45430 (Acid Red 51)
Supplier: National Aniline & Chemical Co.
Name given by supplier: Erythrosin, Bluish (Iodin Eosin)
(Company no longer exists)

Flexo Blue CI 42025 (Basic Blue 1)
Supplier: Salor/Sigma–Aldrich
http://www.sigmaaldrich.com
Name given by supplier: Rhoduline Blue 6G

Patent Blue CI 42051 (Acid Blue 3)
Supplier: Fluka/Sigma–Aldrich
http://www.sigmaaldrich.com
Name given by supplier: Patent Blue V Calcium Salt

Rose Bengal CI 45440 (Acid red 94)
Supplier: Aldrich/Sigma–Aldrich
http://www.sigmaaldrich.com

RP-K™ oxygen scavengers
Supplier: Mitsubishi Gas Chemical America
http://www.mgc-a.com

Tartrazine CI 19140 (Acid Yellow 23)
Supplier: Fluka/Sigma–Aldrich
http://www.sigmaaldrich.com

5. Desenho e aplicação de moldura de baixo oxigénio

Apresenta-se em seguida o artigo publicado referente ao desenho e aplicação de uma moldura de baixo oxigénio, bem como o protocolo desenvolvido que permitiu exibir placas autochrome originais no Metropolitan Museum of Art:

- "Display of Alfred Stieglitz and Edward Steichen Autochrome Plates: Anoxic Sealed Package and Lighting Conditions" (2011). Coautora Katherine Sanderson. *Topics in Photographic Preservation,* Vol. 14. AIC, Washington D.C. pp. 162-167.

DISPLAY OF ALFRED STIEGLITZ AND EDWARD STEICHEN AUTOCHROME PLATES: ANOXIC SEALED PACKAGE AND LIGHTING CONDITIONS

LUISA CASELLA AND KATHERINE SANDERSON

Presented at the 2011 PMG Winter Meeting in Ottawa, Canada

ABSTRACT - Research carried out at The Metropolitan Museum of Art determined the benefits of using low-oxygen conditions for the display of autochromes, when compared to exposure under normal ambient oxygen levels. This work is presented in this volume in the article *Behavior of Autochrome Color Screen Dyes Under Anoxic Conditions* (Casella 2011). The results of this research allowed the Met to exhibit original autochrome plates for the first time in over twenty-five years as part of an exhibition entitled *Stieglitz, Steichen, Strand*. Five autochromes by Alfred Stieglitz and Edward Steichen were displayed in nearly anoxic conditions (0.1% oxygen) for one week in January 2011. Facsimiles were displayed for the remainder of the exhibition.
The following paper highlights the design of an effective low-oxygen sealed package and how it was practically assembled; the light sources used for display; monitoring methodology before, during and after exhibition; and the method employed for facsimile display.

1. INTRODUCTION

The Department of Photographs at The Metropolitan Museum of Art includes in its collection an important group of forty-five autochromes by Pictorialist artists, with iconic images such as Steichen's portrait of Alfred Stieglitz holding a copy of *Camera Work*, or the portrait of Rodin with his sculpture, *The Eve*. Introduced in 1907, autochromes were the first commercially viable color photographic process. Pictorialist photographers were excited by its introduction and used it enthusiastically. However, after 1910, examples of autochromes by these artists are rare, which makes this small collection of photographs from this brief period particularly special.

Previous research on the autochrome process, in particular, the accelerated aging tests carried out by Bertrand Lavédrine (Lavédrine et al. 1993), have made evident the extreme fragility of the dyes present on the autochrome color screen when exposed to light. As a result, the majority of cultural institutions holding autochromes in their collections - including the Met - have established a policy of withholding originals from display, using facsimiles instead (Wagner et al. 2001).

The physical structure of the autochrome is laminar, starting with a glass support, then a first layer of varnish that remains sticky for the application of a layer of potato starch grains dyed red-orange, green, and blue-violet, with carbon black powder to fill the gaps between the grains; a second varnish layer to protect the starch grains from moisture; and a photo-sensitive black and white silver gelatin emulsion. The manufactured plate was then exposed and processed by the photographer, who commonly added a final protective

varnish coating. It is the color screen layer that is the most sensitive to light exposure, and the principal object of this research.

2. LIGHT-FADING EXPERIMENT

Low-oxygen and anoxic environments have long been known to protect certain colorants from light-damage (Arney et al. 1979). Recently there has been a particular focus on the application of anoxia for the exhibition of artworks (Beltran et al. 2008; Townsend et al. 2008).

Experimental research was carried out at the Met, with the supervision of Nora Kennedy and the great support of research scientist Masahiko Tsukada, to determine the effect of anoxia on the light-fastness of the dyes present in the autochrome color screen.

A first experimental phase focused on the six individual dyes comprising the autochrome color screen (Casella 2009) – Erythrosine B, Tartrazine, Rose Bengal, Setoglaucine, Patent Blue and Crystal Violet.

A second experimental phase tested the red-orange, green and blue-violet colorants that result from mixtures of the six individual dyes (Casella 2011). Dye samples prepared following historical formulations, as well as historical study collection autochrome plates, underwent light aging both at environmental oxygen levels and close to anoxic conditions (0.1% oxygen).

The results of the two experiments showed a significant decrease in fading of all the samples under low-oxygen conditions. See article *Behavior of Autochrome Color Screen Dyes Under Anoxic Conditions* in this volume for results on the first experimental phase. The full results of the second experiment will be published in ICOM-CC's 16th Triennial Conference Preprints.

3. EXHIBITION

Five autochromes by Alfred Stieglitz and Edward Steichen were displayed as part of a group of 119 photographs in the exhibition *Stieglitz, Steichen, Strand*. Facsimiles were exhibited for the majority of the show's duration, but with the success of the anoxic light fading tests, the decision was made to display the original plates for seven days during the exhibition – a period of time that falls well within the parameters established as safe by the recent research.

Preparing the original autochromes for display involved creating their low-oxygen packages, carrying out color monitoring of the original plates, and quantifying the light exposure during exhibition.

3.1. Low-oxygen Packages

For the original autochromes, a sealed package was needed that would allow exhibition for a short period of time under low oxygen conditions. A primary goal was to develop a straightforward, economically viable and practical system.

The design was modeled on what has been used at Tate Britain for works of art on paper. The package has two acrylic sheets and an acrylic spacer, which must be the same thickness or slightly thicker than the matted object. Although acrylic is permeable to oxygen in the long term, for short-term use it provides a sufficient barrier. Mitsubishi RP-K™ scavengers were used to absorb any residual oxygen along with Mitsubishi Ageless Eye™ oxygen indicators, which detect levels above 0.1%. A butyl rubber tape was used as the gasket material, which also acted as a sealant that held the package together.

Each autochrome was fitted into a sink mat to hold it in place, leaving a cavity for the scavengers and indicator. Using a glove bag purged with Argon at 45% RH, each matted autochrome was sealed in its package in an environment with oxygen levels below 300ppm. Once assembled, the edges of the packages were clamped for 24 hours to ensure a reliable seal.

These sealed packages were then framed behind a window mat and an additional glazing layer. Since each autochrome was to be displayed behind not one, but two layers of glazing, the decision was made to use non-reflective acrylic for the face of the sealed package and the additional layer. A prototype was assembled using non-reflective acrylic ahead of time to be certain that the butyl rubber would adhere properly to the non-reflective coating on the acrylic.

3.2. Light Sources

Ideally, light sources for autochrome display - as with most works of art - should emit no UV radiation, no heat, and should have a neutral color temperature.

Several light sources were investigated for the display, including LEC panels (Light Emitting Capacitors), which were not bright enough for rendering the details of an autochrome. OLEDs (Organic Light Emitting Diodes) were also considered, but were not available in North America at the time of our research.

The LED “Lite Pad” manufactured by Rosco International was ultimately chosen for use in the exhibition. It is one-quarter inch thick with LED’s (Light Emitting Diodes) around the perimeter and a grid of channels etched into acrylic sheeting to distribute the light evenly. It provides an almost neutral white light, it can be easily outfitted with a dimmer in order to set specific light levels, and it can be ordered in custom sizes.

The Lite Pad has two drawbacks. First, it generates some heat on the surface. Second, even with the dimmer set to its lowest setting, the Lite Pad emits about 500 lux. A simple solution to both problems is to position the Lite Pad at some distance from the artwork to allow for both ventilation and lower light levels.

3.3. Installation

The original works and facsimiles were displayed on a wall with a small interior cavity. A hole was cut in the wall and the framed autochrome hung in front of it. A Lite Pad was mounted behind each work of art inside the wall, on the opposite side of the interior cavity, providing a distance of about twenty-four inches from each autochrome.

For the facsimiles, the Lite Pads remained illuminated constantly while the galleries were open. The only addition to the set-up was a diffusing layer of white vellum paper behind the facsimile, which disguised the grid pattern and edges of the Lite Pad.

For the original plates, the diffusing layer stayed in place and a button was installed in the wall and attached to the Lite Pad, allowing viewer-activated lighting. The light stayed on only while the button was pressed.

4. LIGHT MONITORING

In order to track light exposure, a Hobo U12 datalogger was installed on the inside of the wall beside one of the autochromes – Steichen's *Rodin – The Eve* – facing the light source. The following results reflect the conditions for this particular autochrome, but generally represent the group.

Set to record once per second, the datalogger recorded the level of incident light on the back surface of the wall on which the autochromes were mounted. This light level was higher than the actual light level transmitted through the autochromes. As a result, this data reflects the number of times the button was pushed and the duration, but not the actual light levels on the plate, which were measured through the diffusing layer with a Minolta T-10 Illuminance Meter. In general, the diffusion layer reduced the light level by about 40%.

4.1. Light Monitoring Data

The original autochromes were displayed for seven days. The resulting graphs from the datalogger showed a series of peaks with each peak representing an instance that the button was pressed; the width of each peak indicated the duration of each viewing. With this data, the light dosage for each autochrome was calculated.

Implementation of viewer-activated lighting significantly reduced the overall light exposure. Gallery lights were kept on for a total of 77 hours over the course of the seven days that the plates were displayed. According to the recorded data, the button activating the Light Pad was pressed for just under seven and a half hours. Combined with continuous gallery lighting at 25 lux, the total dosage for the exhibition period was 3,753 lux hours.

5. COLOR MONITORING

Color measurements were taken with a Barbieri Spectro LFP transmission spectrophotometer borrowed from Barbieri Electric. The readings were taken without contact with the plate using standard illuminant D65 and an aperture of 2mm. Five measurements were taken at each measurement site and averaged. On each plate there were between three and five measurement sites.

The overall density of autochromes and the heterogeneous nature of the color screen make obtaining reliable color readings on autochromes difficult on a macroscopic scale. Based on the recent anoxic research, no significant change was predicted. However, if change were to occur, it was expected to appear as fading of the blue starch grains, translated as an increased b* value in the CIE L*a*b* color space.

Despite isolated readings that showed statistically significant change, overall, the results of the color monitoring suggest little or no change to the plates. There was a lack of consistency of results from multiple reading sites on the same plate. The disparity among these results illustrates the difficulty of recording color on these objects.

6. CONCLUSIONS

The *Stieglitz, Steichen, Strand* exhibition was a resounding success, with almost 7,000 visitors attending the show during the week in which the original autochromes were displayed. The publicity this exhibition drew served to focus attention on these unique objects, making it possible to imagine future exhibitions of autochromes for limited amounts of time and providing to the public the irreplaceable experience of viewing originals.

Since the sensitivity of autochromes to light is far too great under normal environmental conditions, it is only the application of anoxic and low oxygen conditions that will make this possible, promising an effective solution to the problem of light-damage during exhibition.

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REFERENCES

- ARNEY, J. S., A. J. Jacobs and R. Newman. 1979. The Influence of Oxygen on the Fading of Organic Colorants. *Journal of the American Institute for Conservation* 18: 108–117.
- BELTRAN, V., J. DRUZIK, and S. MAEKAWA. 2008. An Extended Investigation of the Influence of Oxygen on Color Fading. Poster presented at the *ICOM-CC 15th Triennial Conference, New Delhi, 22-26 September 2008*. Paris: ICOM.
- CASELLA, L. 2009. Autochrome Research at the Metropolitan Museum of Art: Testing Methodology and Preliminary Results for Anoxia Light-Fading. *Topics in Photographic Preservation* 13, comp. B. Bernier and C. Moore, 128-136. Washington D.C.: AIC.
- CASELLA, L. 2011. Behavior of Autochrome Color Screen Dyes Under Anoxic Conditions. *Topics in Photographic Preservation* 14, comp. B. Bernier and C. Moore. Washington D.C.: AIC.
- LAVÉDRINE, B., J.P. GANDOLFO and J.M. SUBSIELLES. 1993. La plaque Autochrome : Analyses Physiques et Chimiques, Étude de la Stabilité des Colorants. In *ICOM-CC 10th Triennial Meeting Preprints, Washington, D.C.*. 1:275–280. Paris: ICOM.
- LAVÉDRINE, B. 2009. *L'Autochrome Lumière. Secrets d'Atelier et Défis Industriels*. Paris: Editions CTHS.
- TOWNSEND, J., S. HACKNEY, J. THOMAS and A. LERWILL. 2008. The Benefits and Risks of Anoxic Display for Colorants. *Conservation and Access*, ed. D. Saunders, J. H. Townsend and S. Woodcock, 76–81. London: IIC.
- WAGNER, S., C. MCCABE and B. LEMMEN. 2001. Guidelines for Exhibition Light Levels for Photographic Materials. *Topic in Photographic Preservation* 9, comp. S. Wagner, 127-128. Washington D.C.: AIC.

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Papers presented in *Topics in Photographic Preservation, Volume Fourteen* have not undergone a formal process of peer review.

6. Conclusão

A aplicação de ambientes de baixo oxigénio apresenta potenciais avenidas para a exibição de bens culturais. O trabalho apresentado permitiu avançar o entendimento das placas autochrome e propôr uma alternativa à anterior norma, insatisfactória, de não exibição de originais. O modelo de embalagem selada utilizado bem como o protocolo experimental proporcionam ferramentas para posteriores estudos semelhantes.

Os componentes de placas autochrome históricas são complexos e contém variáveis devido ao seu percurso (desde o processamento às condições em que foram mantidos ao longo do tempo) que não podem ser equivalentes em absoluto aos materiais criados em laboratório. Ainda assim, o estudo realizado demonstra o benefício da atmosfera de baixo oxigénio em proteger o ecrã de côr das placas autochrome expostas à luz.

Se considerarmos que na maior parte dos casos todos os materiais expostos à luz sofrem, a variáveis níveis, deterioração, podemos arriscar que em toda a exibição de bens culturais existe um equilibrado balanço de decisões curatoriais envolvendo o risco para a peça exposta e o interesse do público. O recurso a embalagens de baixo oxigénio para a exposição de placas autochromes vem propôr, então, uma solução que envolve riscos e um reduzido nível de deterioração. Esta é a decisão que o guardião de qualquer bem cultural toma cada vez que decide expôr um objecto (o que implica necessariamente expô-lo a um mínimo de luminosidade), não obstante tome todas as necessárias precauções de escolha adequada de níveis e fontes de luz e monitorização do objecto.

Podemos concluir que, por isto, que o estudo realizado vem trazer um contributo positivo na apreciação e difusão das placas autochrome para as quais existe agora uma alternativa à escuridão absoluta de não serem exibidas