Chromolithography 1870-1930: The identification of commercial colour lithography processes, ink modifications and conservation

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INTRODUCTION

The research summarised in this poster contextualises chromolithography in the commercial printing trade by the various methods of their production and their ink compositions. Colour lithographic printing, commonly referred to as chromolithography, entered the commercial printing trade in the mid-nineteenth century. The rising demand for colour printing in the twentieth century resulted in more economic and efficient colour printing processes. These demands resulted in an array of new patents for ink formulations, printing papers and photomechanical productions. This research aims to uncover many of the patents, formulas and recipes used in the manufacturing of lithographic inks of the late 19th and early 20th centuries, with a specific focus on additives and modifiers used as driers, extenders and reducers. Information was gathered from relevant patents, treatises, technical manuals, and other historical literature. An overview of published conservation case studies was conducted to understand the potential sensitivities printing inks face. A clearer understanding of the composition of colour lithographic printing inks will serve to inform conservation practice on some of the risks associated with aqueous, solvent cleaning and other treatments.

OVERVIEW OF PROCESS

Chromolithography, photolithography and offset printing are all variants of the original lithography process invented by Alois Senefelder in 1798. While the methods of etching the stone and zinc plate changes, there is no great difference in the lithographic principle, ink process, ink components or the papers printed on.

- Chromolithography is defined as the lithographic colour printing of three or more colours onto a paper substrate. In the creation of early chromolithographs the artist and printer worked together to create the drawing and sequence of colour printing. After the introduction of photographic transfers, images on the plate were prepared by drawing, photographing or transferring.
- Photolithography employs photomechanical means to capture the image on the stone or plate. From patenting or company licensing these process may also be referred to as photo-chromilithography, photochrom, photochromic, photochromie, polychrome and photstint. Trichromatic printing is the name given to the three colour process where often a fourth colour is black (see figure 1). Today this is known as RGB and CMYK colour printing. Halftone is a term used to describe an image that has been turned into a series of dots (see figure 2).
- Offset printing is simply an adaptation of 'direct' lithography. As production speeds increased this method called for its own modified inks often called offset and process inks.

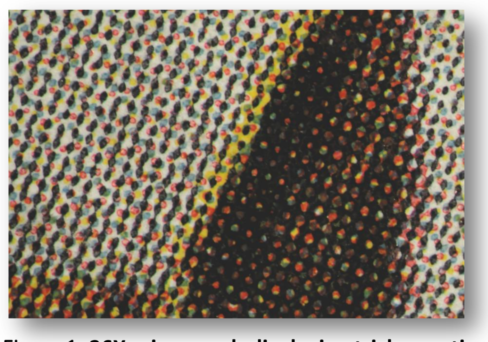

Figure 1: 26X micrograph displaying trichromatic printing (3 colour +black) ©Glenbow Archives – *Calendar collection*

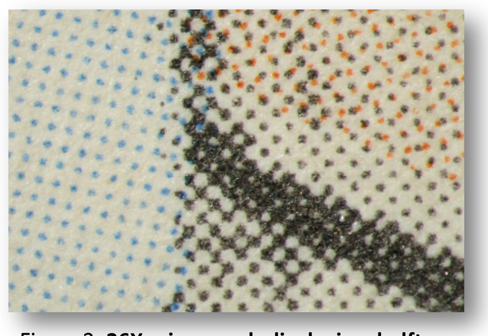

Figure 2: 26X micrograph displaying halftone photography. ©Glenbow Archives – *Poster-125*

MARK-MAKING TECHNIQUES

Many categories of chromolithography are specific to coloured lithographs created with hand drawn marks. This may be difficult to distinguish from the later popular manufactured tint transfer. The table below features a variety of mark-making techniques developed through the decades.

METHOD	DESCRIPTION
Crayon (chalk) manner	This is one of the first techniques used to draw the image on stone (see figure 5)
Splatter method	First described by Senefelder as 'Sprinkled Manner' this technique was a way to produce tone by splattering various sized dots of ink on the stone with a brush
Airbrush	In the 1880's the airbrush was introduced to lithographers in America
Stippling	Similar to stippling in paintings, it became the dominant technique in the latter half of the 19th century. This technique was considered to be a chromolithographic specialty and was mainly used for the creation of tone by creating dots with a brush or pen nib (see figure 7)
TRANSFER METHODS	
Transferring lines and stipple tones from intaglio and lithographic proofs	
Transferring hand drawn work onto textured transfer paper	
Applying tones from commercially produced mechanical tints transfers (or shading mediums). The first patent was granted to Benjamin Day in 1879. By the end of the century there were hundreds of mechanical tints, most of which were largely photographic reproductions of original hand lithographic work making it difficult to distinguish mechanical tints from hand drawn marks (see figure 3 and 6).	

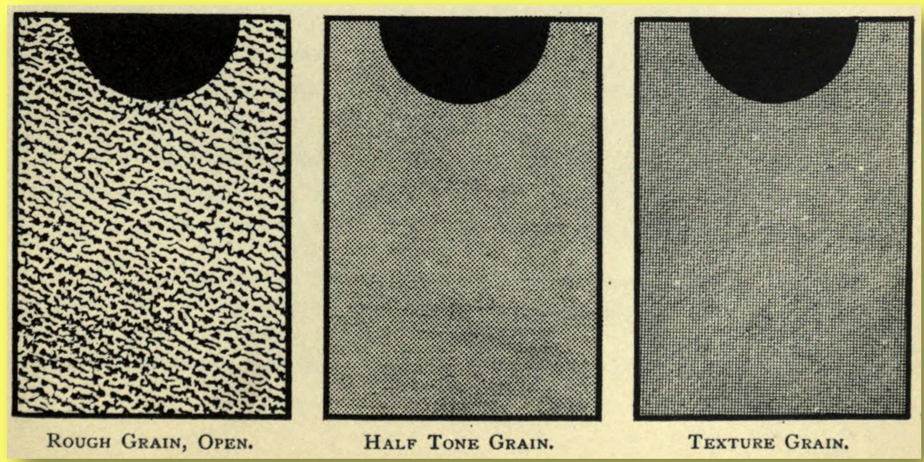

Figure 3: Specimens of mechanical tint transfers in a technical manual[5]

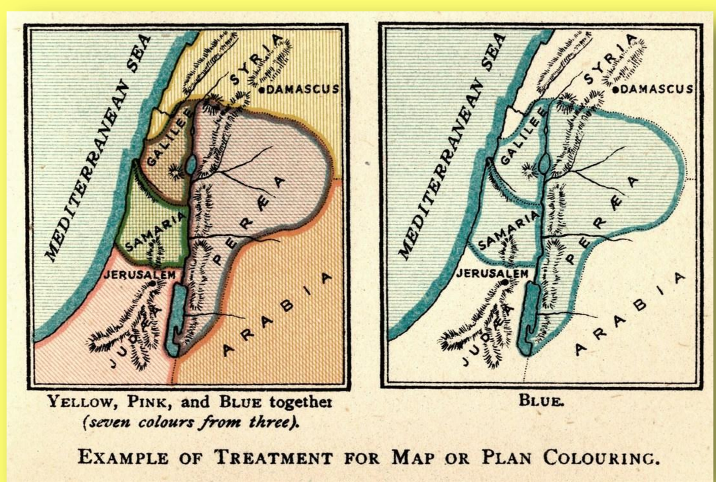

Figure 4: Specimens of ruled line transfers in a technical manual[5]

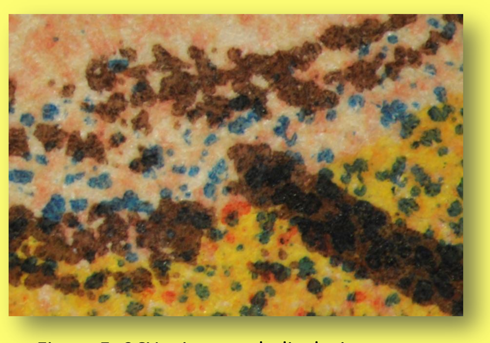

Figure 5: 26X micrograph displaying crayon manner ©Glenbow Archives – *Poster-111*

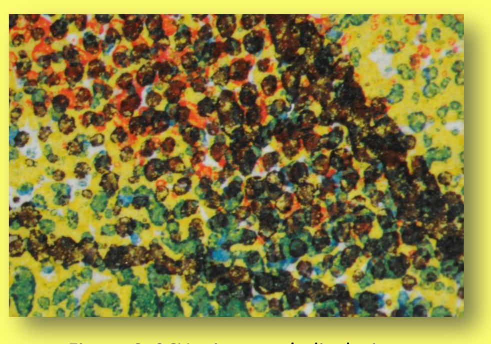

Figure 6: 26X micrograph displaying mechanical tints ©Glenbow Archives – *Death certificate, Henry J. Sullivan fonds*

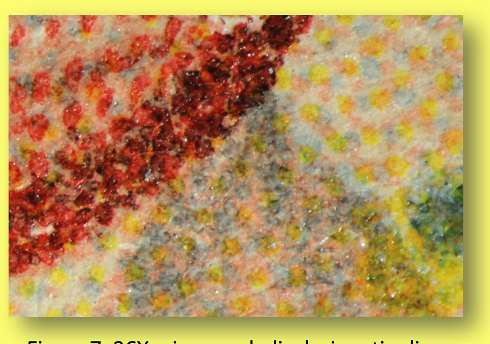

Figure 7: 26X micrograph displaying stippling ©Glenbow Archives – *Marriage certificate, Henry J. Sullivan fonds*

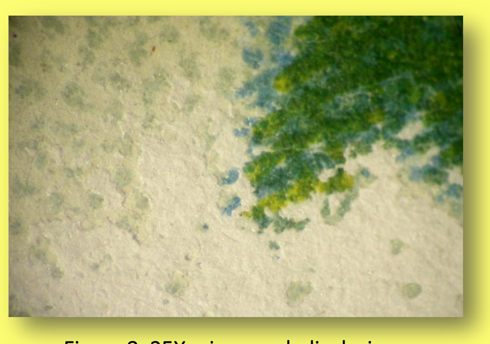

Figure 8: 25X micrograph displaying flaky/powdery ink after aqueous treatment ©Burt Hall Archives

COMPOSITION AND MODIFICATIONS

Lithographic inks were specially formulated for several printing processes but the main components remain to be a pigment/dye mixed in a vehicle with added driers, extenders and reducers. The Vehicle, known as varnish, consists of mainly drying oils, most important being linseed oil. Rosin and rosin oil were first known to be adulterants, but due to the low price became a common addition in many 20th century ink patents. Numerous formulas and patents were recommended as driers. Many of the driers were metallic salts, lead and manganese being most common and cobalt in the early 20th century. It is unlikely that one can determine all the driers as this was ultimately determined by the printer. Extenders are typically of a solid nature and are used to bulk up the ink to increase covering power and decrease the cost. Reducers are generally volatile compounds or oily/fatty substances added to manipulate the consistency and tack of the ink.

DRIER	SHORT DESCRIPTION
Cobalt acetate	The cobalt salt of acetic acid
Cobalt linoleate	See lead/manganese linoleate. By the 1930's it was recommended for use in offset inks as it prevents the paste driers from leaching out[1]
Cobalt resniate	See lead/manganese resinate
Lead (II) acetate (sugar of lead)	White crystalline solid made from lead oxide and acetic acid. It absorbs carbon dioxide, thus becoming basic lead carbonate (lead white). 19th century manuals warned artists its use may cause efflorescence[2]
Lead (IV) acetate (red lead, minimum)	Bright red orange pigment prepared by heating lead monoxide. Insoluble in water and ethanol
Lead linoleate	A powder obtained from saponified linseed oil precipitated with caustic soda and water, added to this was sugar of lead and sometimes litharge[3]
Lead resinate	A powder obtained from boiled caustic soda and rosin, added to this was sugar of lead and rosin soap saponified with litharge[3]
Manganese borate	Consists of borax $Na_2B_4O_7$ precipitated with sulphate of manganese $MnSO_4H_2O$ creating a pure white powder. Considered the most important of manganese compounds used for driers[4]
Manganese linoleate	A powder obtained from saponified linseed oil then precipitated with manganous chloride and water[3]
Manganese resinate	A powder obtained from boiled caustic soda and rosin, added to this is manganous chloride. Soluble in oil when proportions are followed [3]
Terebene/Terebine	Methods vary considerably. One source reported they were prepared by distilling turpentine and sulphuric acid to form a liquid drier for use with other paste or powered driers.[5] Another described a common mixture of linseed oil, lead and manganese compounds in turpentine[3]
Sulphate of zinc (white copperas)	Obtained from sulphuric acid on oxide of zinc
Japanner's gold size (Japan drier, gold size)	Oil boiled with litharge[6] Old drier not used much by 20th century[5]

EXTENDER/ REDUCER	SHORT DESCRIPTION
Alum	Used as an extender
Aluminium hydrate	An extender prepared by adding an aqueous solution of sodium carbonate to aluminium sulphate in water[1]
Beeswax	Wax produced by bees
Calcium carbonate	A white powder used as an extender. Ground oyster shells have been described as a source
Calcium chloride	Used as a gelling agent for starch
Canada balsam	A soft resin addition recommended for bronze-blue ink[7]
Glycerol (glycerine)	A clear hygroscopic viscous liquid. It is produced from the saponification of oils and fats
Lanoline (animal wax, wool wax)	The waxy substance extracted from wool glands
Linseed oil (boiled oil, stand oil)	Boiled oil/Raw oil is a drying oil extracted from the flat plant and processed through several different methods. In dry form it is insoluble in most solvents
Lithopone (orr's white)	A white powder used as an extender . Composed of a mixture of barium sulphate and zinc sulphide. First produced in 1874
Magnesium Carbonate	A white powder. Used to add body to the ink and lower the gloss of coloured inks
Oleic acid	Fatty acid that occurs naturally in almost all animal and vegetable fats and oils
Paraffin oil (mineral oil)	A clear hydrocarbon oil obtained from distillation of the petroleum.
Pomade	Used to inhibit drying of first layer colours such as chrome yellow
Pyroxylin (cellulose nitrate, collodion, nitrocellulose)	Synthetic resin made from cellulose[8]
Stearin	White powder derived from animal and vegetable fats. Composed of glycerides of stearic acid
Sulphur	Used as a reducing agent
Tallow	Processed from animal fat such as beef and sheep. Composed mainly of triglycerides
Tartar (tartaric acid OR cream of tartar)	Applied as a reducer[9]. This is most likely referring to tartaric acid. Soluble in water, ethanol, ether, glycerol. Could refer to potassium bitartrate. Soluble in hot water, dilute acids, alkaline solutions
Thin varnish	A low viscosity oil varnish. Generally when used for printers ink will consist of linseed and/or rosin drying oils
Vaseline® (petroleum jelly)	Translucent semi-solid composition of hydrocarbons. Commonly used by American printers[7]

CONSERVATION ISSUES

Effects of Solvents

- It is thought that the solvents which affect oil paints may also compromise printing inks due to the similar components. The main risks include swelling and softening of the binder from sorption of solvent and the leaching out of low molecular structures in the oil binder[10] – the latter can manifest to an increase in surface roughness and a reduction in glossy sheen. [11]
- SEM images have revealed micro cracks within ink samples that were subjected to acetone and ethanol – no cracks appeared in the water sample, but the author cites tests where water has effected oil films.[12]

Effects of Aqueous Treatment

- Saponification reactions on the oil binder are known to occur in alkaline conditions where a metal alkali acts upon a carboxylic or fatty acid in the presence of water – this risk increases above pH 8.0. Analysis has indicated this may arise in printing inks which have been exposed to aqueous solutions of calcium hydroxide forming calcium crystals at the surface.[12] It is possible this reaction may be one cause of media loss seen in Fig. 8. During aqueous washing the fillers (metallic salts) within the paper substrates potentially displaced and acted upon the oil structure creating water soluble soaps within the printing ink.
- Coloured inks have been known to become soluble during aqueous washing despite being stable during pre-testing. One conservator reported a green dye leeching due to a drop in pH of the wash water during aqueous treatment.[13] Another reported the migration of an orange component within the ink during aqueous treatment.[14]

Other Conservation Issues

- Inks displaying haloing caused by the leeching of oil through the substrate could be more vulnerable to offsetting or aqueous/solvent treatments. The haloing could be a consequence of adding non-drying oils to the inks creating a potentially weak bond with the substrate as they migrate. Blanching has been observed on black printing inks.[15] This could be caused by the mobility of the free fatty acids migrating to the surface.
- Recent research suggests that additives, particularly lead pigments and driers, have more influence on the ageing characteristics of linseed oil than the rate of heating. Analysis determined that oil samples treated with lead driers and heat displayed higher rates of hydrolysis than those treated with only heat.[16] While this is ongoing research it may have implications for printing inks where lead based driers or pigments are present.

Acknowledgements:
The author would like to thank Dr. Jane Colbourne of Northumbria University for the expert guidance and consultation in this research project and the Glenbow Museum for giving the opportunity to survey their collection.

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