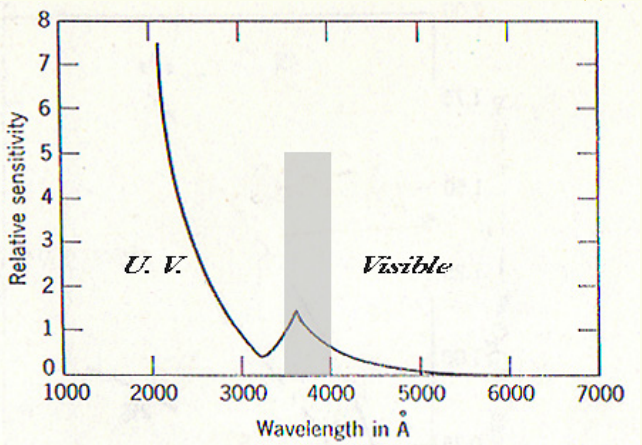
## SENSITIVITY OF DICHROMATE - heliogravure/gum

Chromium salt has a long, straight exposure curve and it is important to make the most of it, learning where and how to mediate among the perfection of the tonal transitions, the length of the exposure time and one's own technical experience and instrumental equipment.

We have already mentioned the relative sensitivities of Potassium and Ammonium salts, the latter being about one third faster than the former. Now we will touch upon the working wavelength, the effects of chromium concentration, contrast modulation and shelf life of the Carbon Tissue; characteristics that are similar for the two salts.

### WAVELENGTH (λ)

The peak of sensitivity with respect to the radiation wavelength, is between 360 and 400 nm (3600÷4000Å), which means in the nearby U.V. (known as UV-A) (1). For the behaviour of the various U.V. light sources, refer to the extremely comprehensive article at ***https://sandykingphotography.com/resources/technical-writing/uv-light-sources-for-printing*** dated 2001, while for more recent tests with LED light, see ***https://carlesmitja.net/2020/07/28/heliogravure-xii-led-uv-lighting/*** .

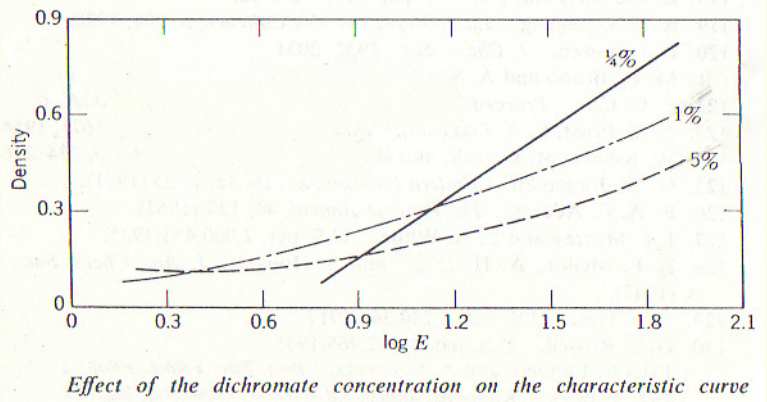



*Spectral sensitivity of dichromated colloids*

All useful light sources provide an emission focused on this range with variations in curve contrast. As in traditional photography, a point source such as arc or mercury lamp, generally produces more contrasted images while diffuse widespread radiation,- such as fluorescent tubes or LED strips, generates softer images. There are also LED sources with emitters grouped and focused by a parabola, which are therefore very close to a point source. ... Each method merits experimentation.

### CONCENTRATION ▶ contrast (2)

The concentration of chromium salt in the sensitised layer will affect the contrast in the final image. Really this is the surest way and controllable choice to modify the curve. In particular **a low concentration of $Cr_2O_7^{2-}$ provides more contrasted images, while a higher one gives softer images**, unfortunately <u>flattening in particular the tones in the low exposure times of the sensitive layer</u> as shown in the side diagram.

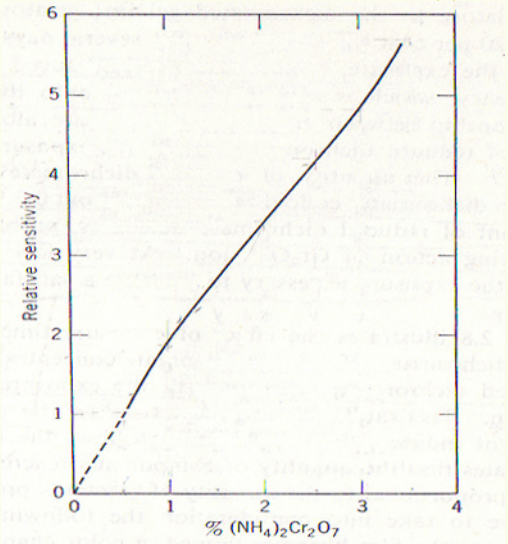



*Effect of the dichromate concentration on the characteristic curve*

This means that at the highest densities values of the film – which by exposure produce on the Carbon Tissue thin insoluble thicknesses of gelatine – very close density values will be obtained, making it difficult in the print to split the tones; see in the graph the 5% dichromate dashed line. **These low thicknesses are**

**the shadows in *heliogravure***, which are quickly bitten during the acid action and tend to be compressed.
On the contrary, in negative film techniques such as '*gum dichromate*', these thin thicknesses correspond to the highlights, which will therefore suffer from such flattening using high concentrations of chromium salt.

An average contrast value is considered a concentration of 2.5% of $Cr^{6+}$ in the dried layer, corresponding to a 2 grade of traditional enlargers photo paper.

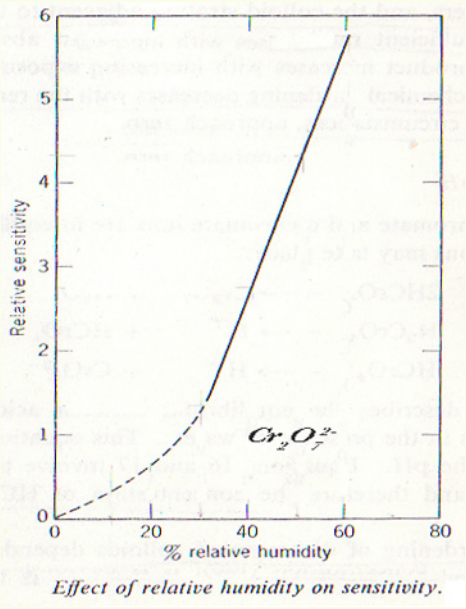


*Relation between the concentration of dichromate and relative sensitivity.*

CONCENTRATION ▶ sensitivity

The concentration of the sensitiser affects the exposure time too. In particular, **the sensitivity increases together with the salt concentration**, i.e. to obtain the same densities on C.T. and later the corresponding ones in printing, a 3% sensitised layer must be exposed less time than a 2% one.
On average, the *slope* of the curve (as properly said) is about 1.7. This means that for a variation of 1% on the salt concentration, the exposure varies (roughly) by 1.7 times.

E.g.: If a 3% $Cr^{6+}$ concentration requires an exposure time of 8', a 4% concentration will require approximately 4' 45" (= 8 : 1.7).



*Effect of relative humidity on sensitivity.*

SENSITIVITY ▶ moisture

It has been mentioned that the $Cr^{6+}$solution spread on paper acquires sensitivity while drying, but also the perfectly dry salt shows no sensitivity to light radiation (3).

A certain degree of humidity must therefore be maintained in the sensitised gelatine layer once dry; the response to UV light radiation measured between 30% and 60% of relative humidity, shows a greater sensitivity to the increase in humidity of the layer, with a noticeable difference between the extreme values measured.

For this reason it is preferable to rely on a hygrometer during the drying phase.

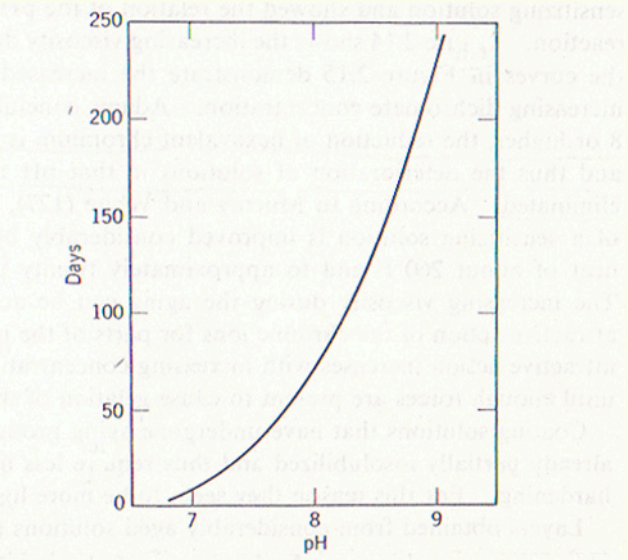
DARK REACTION

A final consideration about the sensitivity of chromium salt concerns a reaction that takes place on C.T. in the contact between the salt itself and the proteins contained in the '*colloid*' (4). This reaction is called *dark reaction* because it happens even in the dark for pure 'ageing', more or less fast, according to storage conditions of the sheet once sensitised; that is to say that it happens anyway!

It consists in a shift of the equilibrium $Cr_2O_7^{2-} \leftrightarrows CrO_4^{2-}$ forming a much less sensitive salt, the *chromate*. A decrease in temperature slows down the reaction, as well as an increase in pH. Therefore, wishing to prepare in advance several sheets of sensitised Carbon Tissue to use it

days later, it is better to keep the sheets sealed one by one, in the refrigerator.
The increase in pH is even more effective for long storage, but decreases the sensitivity, forcing an increase in exposure time. It also introduces the need of pH value control.

The best solution, therefore, is to prepare the sensitised C.T. in needed quantity for the next 48 hours and expose/strip it within the same time interval from preparation. Its natural pH is slightly below 7.



*The effect of pH on the useful life of dichromated glue solution at room temperature.*

- All considerations also apply to dichromated gum emulsions.
- The diagrams come from:

**J. Kosar - *Light Sensitive Systems*** - *Chemistry and Application of non Silver Halide Photographic Processes* - Ed. Jhon Wiley&Sons, 1965

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*1) UV-A radiation is much less dangerous of that at λ < 300 nm (UV-B). Use anyway sunglasses even when looking at the reflected emission*

*2) 'Chromium concentration', 'bichromate' or 'sensitising concentration ', will here always mean the weight in grams of the whole salt, this being a more elementary number to work with and which does not have any consequences once dilution and exposure standards have been set. Actually, the true concentration of $Cr^{6+}$ depends on its percentage weight within the whole molecule: 35% in the case of $K_2Cr_2O_7$ and 41% in $(NH_4)_2Cr_2O_7$. See also footnote (2) in 'SENSITISING - heliogravure'.*

*3) The raw material is stored in the dark anyway, to avoid that any moisture present or introduced during the handling, can make over time a partial reduction of salt ($Cr^{6+} \rightarrow Cr^{3+}$). Chemical reactions are mostly mediated by water !*

*4) The proteins the gelatine is made of, are the stuff that undergoes oxidation (i.e. 'tanning', 'hardening') during exposure or ageing. The same happens to traditional Ag-salts film, which are mixed in the same animal gelatine; the Silver films build a 'veil' after a quite-some storage life, although much longer time than C.P. In fact silver halides are not as 'oxidizing' agents as the hexavalent chromium !*