Historical Evolution of the Champagne Bottle Coloration during the XXth Century

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The main event of the beginning of the XXth century in bottle glass making is the automation of the process. It induced some adjustments of the glass composition but the green coloration was still obtained via several percents of iron oxide. The stabilization of the glass composition around 1950 was followed by changes in the colouring system. During a first period the glass is oxidized by additions of manganese oxide and later on, of potassium dichromate, this last compound producing a green colour typical of Cr^{III}. Iron oxide is progressively replaced by chromium oxide in order to decrease the IR absorption by the molten bath and make the melting process easier. During the last period, a major change occurs : transition from oxidized glasses to reduced ones, thus ensuring simultaneously the elimination of Cr^{VI} from the glass and very good anti-UV properties necessary for the storage of Champagne wine.

Before the mechanization

"The main quality of bottles is their strength ; it is nearly the only one which was considered as important and, as soon as the brown or greenish colour was clean and not cloudy, and the bulk roughly without bubbles, nobody minded the variations of colour intensity. This colour depended mainly on the nature of the raw materials which were used and that depended on the location of the factory.", wrote G. Bontemps in 1868[1]. In the nineteenth century, each factory has its own glass composition. Their main features are their high alkaline-earth content and the very high iron oxide content (Table 1) : it was obtained through the use of what we would call "poor quality" raw materials, sand and limestone mixed with earth and organic , unleached soda ash, clays… all that giving a low cost glass. In spite of the strange chemical composition compared to the usual present soda-lime-silica glass, those glasses presented adequate properties : an easy melting, a good forming behaviour even if they were very easily devitrified and quite good chemical properties towards wine[2].

Wt %	Maumené - 1862	J. Henrivaux[3]- 1897 –Vauxrot	Vauxrot 1947	Vauxrot 1962	Vauxrot 1968	Oiry -1983
SiO_2	58.4	59.7	67.5	69.5	69.5	71
CaO	18.6	21.4	9.8	11.5	12.5	12
MgO	0	8.0				
K_2O	1.8	0				
Na_2O	9.9	6.1	15.0	15.0	14.0	14.5
Al_2O_3	2.1	2.39				
Fe_2O_3	8.9	2.21	3.0	1.0	0.5	0.3
MnO_2			1.5	0.1	< 0.1	< 0.1
Cr_2O_3				0.07	0.12	0.12

Table 1 – Chemical composition of glasses

At the end of the nineteenth century the chemical composition had notably changed : the iron oxide content was lowered (Table 1) and some magnesia added to the batch. Most probably the devitrification problem was still more difficult to manage but "this glass had another quality which was that it hardened very quickly during the cooling down, making the forming process easier for the glass makers and making this operation much more economic because they were obliged to proceed very quickly"[4]. The lower iron oxide content gave a lighter glass (Figure 1).

Changes following the forming process mechanization

The beginning of the twentieth century saw the mechanization of bottle glass making and the glass chemical composition had to be changed to adjust to the forehearth process[5]. The colour of the glass remained based upon iron oxide oxidized by manganese oxide additions. In 1947, the Vauxrot Champagne glass composition (Saint Gobain) was basically a classical soda – lime – silica glass (table 1 and figure 2). Manganese oxide ensured the oxidation of iron in the glass, conferring to it some ultra-violet absorption needed to keep the wine in good conditions (Figure 1 – 2.95% Fe_2O_3 – Spectra are calculated).

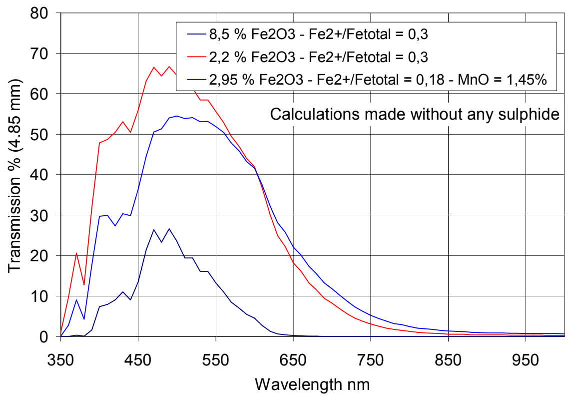


Figure 1 - Glass transmission before and immediately after the mechanization process

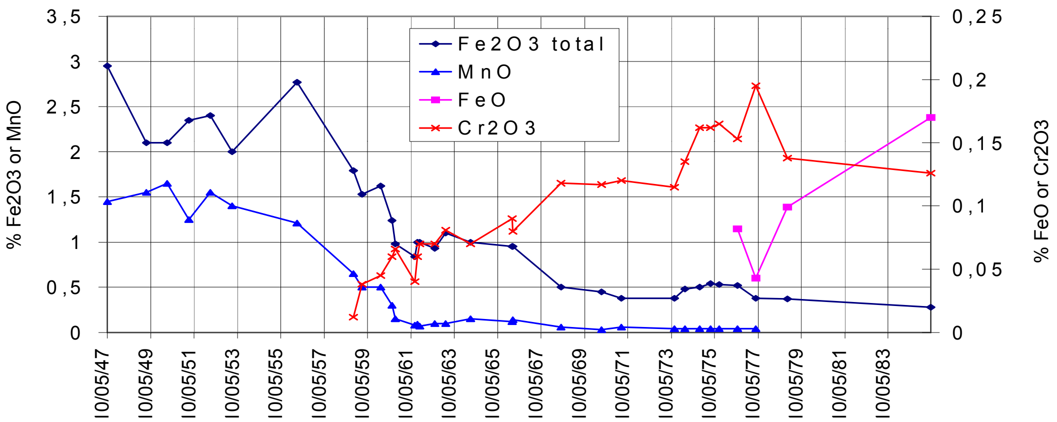
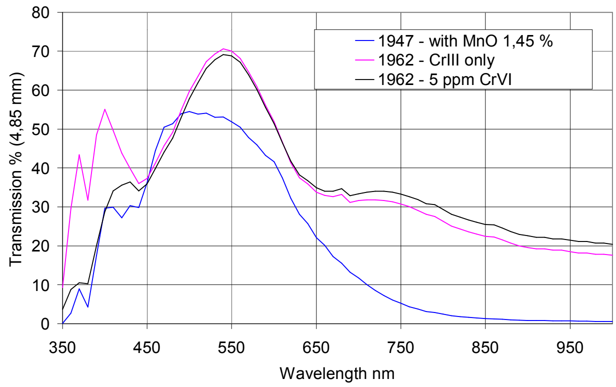


Figure 2 - Evolution of the coloring system after the mechanization process

Around 1956, History caused a change in the bottle glass composition : Morocco became independent and the cost of manganese oxide rose very fast. Thus, the previous oxidizing agent was slowly replaced by potassium dichromate (Figure 2). In the analysis of 1962, there is 0.1 % of manganese oxide and 0.07 % of chromium oxide combined with 1 % of iron oxide in Vauxrot Champagne glass composition (Figure 3 – 1962). Potassium dichromate brings Cr^{III} and most probably some Cr^{VI} which has a striking effect on the absorption curve in the near UV region even at very low concentration (Figure 3 – Cr^{III} only and 3 - 5 ppm Cr^{VI}). The presence of this low Cr^{VI}-content is sufficient to recover the UV – protection offered by 2.95% of iron oxide + 1.45% of manganese oxide in the composition of 1947. At the end of this period, potassium dichromate was substituted by iron chromite. The replacement by iron chromite does not ensured the anti-UV efficiency, the glass being less



oxidized (Figure 3 – curve Cr^{III} only).

In 1968, half of the remaining iron oxide is replaced by chromium oxide : the colour is not so different but the absorption curve is. The IR - absorbing Fe^{2+} is replaced by Cr^{3+} which does not absorb in the IR region, making easier the thermal transfer and thus the melting process (Figure 4 – 1962 and 1968). No particular change occurs between 1968 and 1972 except the stabilization of the chemical composition with silica - and lime - contents significantly higher than before which indicates a higher forming speed, the viscosity curve being steeper.

From an oxidized glass to a reduced one in the 1980's

The last major evolution of the glass composition takes place in the 1980's with the transition from oxidized glass to reduced glass. The anti-UV absorption is ensured by iron sulphides instead of Fe^{III} (or Cr^{VI} which was thought about as very efficient, but rejected due

Figure 3 - Transmission of glasses with and without Cr^{VI}

to refining problems met with highly oxidized glasses) (Figure 5 – 1978 and 1985). This allows the decrease of the total iron oxide content down to 0.3 % (table 1 and figure 2). The

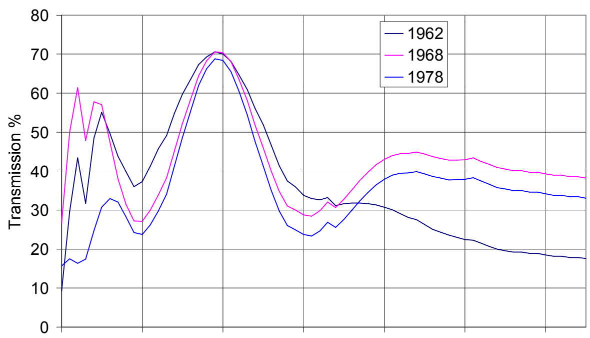


Figure 4 – Iron oxide replaced by chromium oxide

FeO content increases (0.1 up to 0.17 %), the new Fe^{2+}/Fetotal ratio being around 0.6 or 0.7. Another advantage of this change is the total disappearance of Cr^{VI} from the glass compositions, this element being recognised a few years later as toxic contrary to Cr^{III}.

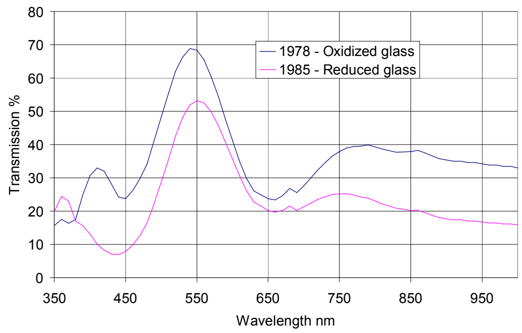


Figure 5 - From an oxidized glass to a reduced glass in the 1980's

Nevertheless, amber glass has always had a poor reputation with glass makers, not because of fining problems, but because of melting and re-boiling problems : the low sulphate-content and high reducing agent-content in the batch oppose the sulphate homogenizing reactions. Glass makers had to learn how to work with this kind of glass at the usually high pull rates in bottle glass making. It should be noticed that it was also during those few years that recycled cullet began to be widely used in bottle glass furnaces and this also means a very efficient stirring[6]. It was made possible most probably by the use of very efficiently stirring furnaces.

At the beginning of the twenty first century, Champagne bottle glass has not changed very much since the 1980's. The anti-UV protection has been reinforced by minor modifications of the sulphide content in order to met the requirements of the customers who, more and more often, sell their product in the highly lighted supermarkets.

Conclusion

As a conclusion, figure 6 presents the colour evolution on the a* - b* diagram : the story of Champagne glass colour could be considered as an exercise in glass formulation. The colour obtained by the various systems has always been very similar but its intensity has considerably increased during this period.

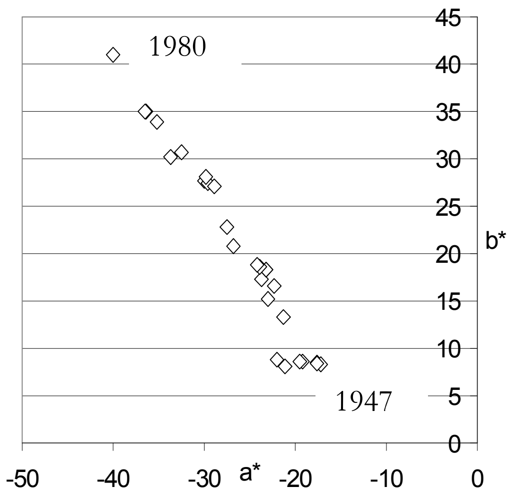


Figure 6 - a*, b* evolution during the period 1947 - 1980

The transmission spectra presented in this paper were calculated from the chemical analysis periodically made and recorded by the analytical group in Saint-Gobain Recherche since 1947 up to our days on Champagne glasses made by the Vauxrot bottle plant and later by the Oiry bottle plant of Saint-Gobain Emballage.

The oxydo-reduction states are not known for the earlier glasses and therefore, some approximations were made about the ratio Fe^{2+} / Fe^{3+} taking into account the batch composition.

General information about the various historical evolutions and their reasons was asked for and very friendly given to me by people from Saint-Gobain Emballage and others. Many thanks to all of them.

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[1] G. Bontemps, *Guide du verrier* (Librairie du dictionnaire des arts et manufactures, Paris, 1868), p. 498.

[2] M-H. Chopinet, Verre **6[5]**, p. 63 (2000).

[3] J. Henrivaux, in *Le verre et le cristal* (, Paris, 1897).

[4] L. Appert, J. Henrivaux, in *La verrerie depuis vingt ans* (, Paris, 1894).

[5] M-H. Chopinet, *Champenoises, Champagne 2000* (Atelier-Musée du verre de Trélon, Fourmies, 2000), p. 114.

[6] M-H. Chopinet in *XIX International Congress on Glass,* 2001, edited by Society of Glass Technology, .