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Black chromium coatings: experimental and calculated optical properties using inhomogeneous medium theories

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Résumé. — On présente la caractérisation détaillée (propriétés optiques, composition en volume, structures en surface et en volume) de revêtements sélectifs de chrome noir utilisés pour la conversion héliothermique. Un modèle des propriétés optiques prenant en compte tous ces paramètres est ensuite développé à partir des théories de Maxwell Garnett et du Milieu Effectif permettant la détermination d'une constante diélectrique effective dans les milieux inhomogènes et rugueux. On étudie l'influence de rugosités présentant différents profils. On compare les comportements optiques déduits des diverses théories et on discute les limites d'application de ces théories.

Abstract. — Bulk composition, surface and volume structures and optical characterization of selective black chromium coatings used for photothermal conversion of solar energy are presented. A model of the optical properties, taking into account all these parameters and using Maxwell Garnett and Effective Medium Theories for the determination of an effective dielectric constant for the inhomogeneous and rough media, is then developed. The influence of different roughness profiles is considered. The optical behaviour obtained with the different theories is examined and the limitations of these theories are discussed.

1. Introduction. — The interest of black chromium coatings on metallic substrates as selective absorbers for the photothermal conversion of solar energy at low and intermediate temperatures (≤ 200 °C) has been well demonstrated [1]. Their industrial technique of deposition: electroplating, their excellent spectral selectivity, their high thermal and mechanical stability and consequently their good cost efficiency ratio have to be especially emphasized. Many works have already been published on this subject [2-7]. Only one of them [2] tries to go further than a qualitative explanation of the selectivity and develops a quantitative model. This last step is absolutely necessary, not only in order to understand the optical behaviour of these black coatings, but also to define exactly some important parameters of the low and intermediate temperature selectivity in order to use them later at higher temperatures with other materials.

We present here, a complete quantitative characterization (§ 3) of the black chromium coatings prepared at C.E.N.G. [8] including: composition, volume and surface structures, and optical properties. Taking into account the surface roughness and the variations of structure and composition inside the film, we develop a model of calculation of the optical relectivity of the coating (§ 4) using an effective dielectric constant for each of the elementary granular layers (of given composition) into which the coating has been divided. This dielectric constant is deduced from inhomogeneous medium theories which are briefly presented (§ 2). The optical behaviour obtained with the different theories are compared with experimental results and the limitations of the theories are discussed (§ 5).

2. Inhomogeneous medium theories. — In order to compute an effective dielectric constant for the inhomogeneous media, we investigate the well-known Maxwell Garnett theory [9, 10], a slightly improved version of which [11, 12] allows account to be taken of high densities of included particles, and the self-consistent theory [13] first developed by Bruggeman [14]. In both theories we have made the assumption of ellipsoid-shaped particles introduced by Cohen et al. [15].

Both theories have to express two quantities at the beginning of their development:

— the space-averaged field $E_i$ inside an ellipsoidal inclusion of complex dielectric constant $\varepsilon_i$, embedded in a surrounding medium of complex dielectric cons-


tant $\varepsilon_{\text{out}}$. $\mathbf{E}_i$ is the sum of the electric field $\mathbf{E}_0$ in the surrounding medium and of the depolarizing field $\mathbf{E}_p$ due to the polarization $\mathbf{P}$ of the ellipsoidal inclusion:

$$\mathbf{E}_i = \mathbf{E}_0 + \mathbf{E}_p$$

(1)

$$\mathbf{E}_p = -g \cdot \frac{1}{\varepsilon_{\text{out}}} \mathbf{P}$$

(2)

$$\mathbf{P} = (\varepsilon_i - \varepsilon_{\text{out}}) \mathbf{E}_i.$$  

(3)

It follows that

$$\mathbf{E}_i = \frac{\varepsilon_{\text{out}}}{g\varepsilon_i + (1 - g) \varepsilon_{\text{out}}} \mathbf{E}_0$$

(4)

where $g$ is the depolarization factor along the applied field (if the inclusion is spherical $g = 1/3$). These relations, written independently of time and space, assume that $\mathbf{E}_0$ is static and uniform. The origin of $\mathbf{E}_0$ being the dipolar field of all other particles induced by the applied field $\mathbf{E}_{\text{ext}}$, the physical limits of the theories can be deduced from these conditions on $\mathbf{E}_0$: inclusions have to be small compared to the wavelength of the incident radiation so that a quasi-static approximation may be used; inclusions have to be distant enough from each other so that the multipolar field interactions can be neglected;

— the second quantity is the average field $\mathbf{E}_{\text{av}}$, in the inhomogeneous medium, which is defined as the spatial average of the static and uniform field in the inclusions $\mathbf{E}_i$ and in the matrix $\mathbf{E}_m$ of complex dielectric constant $\varepsilon_m$:

$$\mathbf{E}_{\text{av}} = q\mathbf{E}_i + (1 - q) \mathbf{E}_m$$

(5)

where $q$ is the filling factor of the medium (inclusion volume over total volume).

### 2.1 Maxwell Garnett Theory

Maxwell Garnett theory (Fig. 1) assumes that each inclusion is embedded in the real matrix so that the influencing field $\mathbf{E}_0$ is the electric field in the matrix itself $\mathbf{E}_m$ and $\varepsilon_{\text{out}} = \varepsilon_m$ in eq. (4). Writing now eq. (5) with the displacement $\mathbf{D}$, one defines an average dielectric function $\varepsilon_{\text{av}}$:

$$\begin{cases} 
\mathbf{D}_{\text{av}} = q\mathbf{D}_i + (1 - q) \mathbf{D}_m \\
\varepsilon_{\text{av}} \mathbf{E}_{\text{av}} = q\varepsilon_i \mathbf{E}_i + (1 - q) \varepsilon_m \mathbf{E}_m 
\end{cases}$$

(6)

(7)

it follows from (4), (5), (7):

$$\varepsilon_{\text{av}} = \varepsilon_m \cdot \frac{\varepsilon_i (g + q (1 - g)) + \varepsilon_m (1 - q) (1 - g)}{\varepsilon_i g (1 - q) + \varepsilon_m [1 - g (1 - q)]}$$

(8)

which reduces to the well-known Maxwell Garnett formula when $g = 1/3$. This formula is non-symmetric in $\varepsilon_i$ and $\varepsilon_m$; it is thus clear that, whatever the filling factor, the behaviour predicted by the Maxwell Garnett theory for the material will be similar to that of the pure matrix. Consequently, this theory cannot account for the percolation phenomenon, i.e. the passage from a dielectric to a conducting behaviour (or reciprocally) at a given filling factor.

### 2.2 C.C.C.A. Model

In order to account for this change in behaviour observed in the electrical and optical properties of inhomogeneous media at a critical value $q_c$ of the filling factor, Cohen et al. [15] (C.C.C.A.) have proposed simply to exchange the inclusion and the matrix dielectric constants and change $q$ into $(1 - q)$, considering that beyond $q_c$ the inclusions are in contact with each other and begin to act, as a matrix, whereas the matrix begins to act as isolated inclusions.

Using resistor network models, several authors [11, 12, 16] have calculated the value of $q_c$ corresponding to the percolation threshold in relation to the geometry of the material. For a two dimensional system with metallic inclusions, $q_c$ is about 0.30 whereas it decreases to 0.16 for a three dimensional system.

### 2.3 Effective Medium Theory

In this theory, first developed by Bruggeman [14], both the matrix and the inclusions are considered as small spheres (or ellipsoids in a more general case) occupying the whole volume of the material (Fig. 2). Under these conditions, the field influencing the two types of spheres is the average field $\mathbf{E}_{\text{av}}$ and $\mathbf{E}_0 = \mathbf{E}_{\text{av}} \varepsilon_{\text{out}} = \varepsilon_m$ in eq. (4), while eq. (5) giving $\mathbf{E}_{\text{av}}$ remains unchanged.
This assumption ensures the self-consistency of the theory and leads to eq. (9):

\[(1 - g) \varepsilon_{av} + \varepsilon_{m}(\varepsilon_{av} - g) + \varepsilon_{m}(g + q - 1) - g\varepsilon_{l} \varepsilon_{m} = 0 \quad (9)\]

where the symmetry of the roles played by the inclusion and the matrix is obvious. Eq. (9) being quadratic in \(\varepsilon_{av}\), the choice between the four possible solutions for \(\varepsilon_{av} = \varepsilon_{1av} + i\varepsilon_{2av}\) is not obvious. This point will be discussed elsewhere [17]. Bruggeman’s symmetrical theory predicts a percolation threshold for a filling factor \(q_{c} = 0.3\) in the case of spherical metallic inclusions. One should notice that some authors [18, 19] observed large discrepancies between this theory and experiment.

3. Characterization of the black chromium coatings.

All the investigated samples were prepared by electroplating in a chromium bath free from sulphates, at the C.E.N.G. [8]. Among the various parameters entering this method, the deposition time has a major effect on the composition of the deposit. It has been shown [8] that the deposit weight goes through a minimum at 90 s, all other parameters being fixed. Furthermore, we have noticed that this deposit exhibits the best selective optical properties [20]. The samples which are presented here, and for which we have developed an optical model, were deposited under these optimal conditions on chemically cleaned copper substrates either uncoated (samples 1) or covered with a thick nickel underlayer of about 10 µm (samples 2). The characterization of these two types of deposits given below result from measurements on four samples of each type at least. The observed spread among each type is less than 2 %, the homogeneity of each sample being about 1 %.

3.1 Surface structure. — Scanning electron microscopy performed on samples 1 and 2 shows a random roughness of about 0.2 µm in period and 0.1 µm in height (Fig. 3a), which appears to be intrinsic to the deposition technique. As a comparison, this small intrinsic roughness is still present on samples deposited on very rough steel substrates, superimposed on the substrate macroroughness (1.8 µm period, 1 µm height) (Fig. 3b).

3.2 Composition and volume structure. — Photoelectron spectrometry (ESCA) associated with a thinning down technique by ionic bombardment shows a composition varying with depth: the first 200 Å consist in a mixture of \(\text{Cr}_2\text{O}_3\) and \(\text{CrO}_3\) in similar proportions. Beyond 200 Å from the air interface and up to 1 000 Å, the major constituent is the oxide \(\text{Cr}_2\text{O}_3\) with slight traces of metallic chromium. Between 1 000 and 3 000 Å, the coating consists of a mixture of \(\text{Cr}_2\text{O}_3\) and metallic chromium the proportion of which decreases down to the substrate. The metallic chromium concentration represented by the filling factor \(q\) (or volume fraction) varies with thickness as shown in figure 4. It is important to note that the thickness of the upper oxide layer, and consequently the whole thickness of the coating, is quite uncertain because the behaviour of a rough surface under ionic bombardment is not known. The repro-

Fig. 3. — Scanning electron microscopy (G = 10 000) on the surface of a black chromium coating deposited on : a) bare copper substrate; b) nickel plated copper substrate.

Fig. 4. — Variations of the Cr filling factor \(q\) inside the coating versus thickness, deduced from ESCA measurements.
ductibility of these profiles on different samples of each type (1 or 2) is however very good.

Electron microscopy, performed after thinning down the substrate by ionic bombardment, shows roughly spherical inclusions of about 100-200 Å. Electron diffraction confirms the nature of the inclusions: f.c.c. metallic chromium. A thicker coating obtained after ten successive similar treatments was examined by X-ray diffraction, and the observed line broadening confirms the mean value of 100-200 Å for the crystallite size.

3.3 Optical characterization. — Two types of optical measurements have been performed, as a function of wavelength from 0.35 to 15 µm on these light-scattering coatings:

— hemispherical reflectivity as a function of angle of incidence and polarization, with a spectrophotometer equipped with two integrating spheres covering the entire spectral range acting simultaneously as source and sample holder;

— bidirectional reflectivity for a given incidence in order to characterize the angular dispersion induced by surface roughness. The apparatus, the measurements and their accuracy have been presented in detail in a previous paper [20].

The angular dispersion of the normalized reflectivity of samples of type 1 and 2 and of a specular Au mirror has been measured around the angle of specular reflection for radiation incident at an angle \( \theta = 15^\circ \) and wavelength \( \lambda = 4 \mu \text{m} \). The curve (Fig. 5) relative to the Au sample is characteristic of the instrument function, it exhibits a width at half height \( S_0 = 1013' \). The same quantity determined for sample 1 (black chromium on copper) and sample 2 (black chromium on nickel plated copper) is \( S_1 = 1016' \) and \( S_2 = 1019' \). This weak scattering of a few minutes nevertheless induces a significant difference (about 2%) between the solar absorptance value deduced from the specular reflectivity measurement in the \( \theta \)-direction and that deduced from the corresponding hemispherical reflectivity. This fact will be taken into account in the interpretation of the optical model results.

The hemispherical reflectivity of samples 1 and 2 has been measured from 0.35 to 15 µm for radiation incident at an angle of 20°. The results plotted in figure 6 show a similar behaviour in the visible range in the two cases, while the coating deposited on bare copper (sample 1) exhibits a better behaviour than the one deposited on nickel plated copper (sample 2) in the infrared, i.e. a higher reflectivity and threshold at lower wavelength.

![Fig. 5.](image)

From these optical results, even if the composition and the structure of the coatings are known, it is impossible to determine the influence of the various parameters (thickness of the different layers, dielectric constant of the components, chromium filling factor, characteristic dimensions of roughness...) on the optical properties in the absence of any optical model.

4. Optical model. — We have developed an optical model for the coatings deposited on copper and nickel-plated copper. The system has been divided
into four parts to which we have applied adequate treatments:
- a first part consisting in a rough Cr₂O₃ layer of 1 000 Å thickness;
- a second part of 3 000 Å cermet-like material: Cr inclusions in a Cr₂O₃ matrix with a filling factor following the variation deduced from ESCA measurements (Fig. 4);
- a third part, in the case of nickel plated copper substrate only, of 400 Å cermet-like layer just covering the substrate, accounting for the small roughness of the thick nickel layer;
- a last part being either the bulk copper substrate itself or the thick (opaque) nickel layer.

All these parts, except the last one, are inhomogeneous. In fact, one can consider the external roughness as Cr₂O₃ inclusions in an air matrix and the internal one as Ni inclusions in an already inhomogeneous medium (Cr/Cr₂O₃ cermet). Each part has been divided into sublayers of 50 Å thickness in which the inclusion filling factor can be considered as a constant. The inhomogeneous medium theories presented in § 2 have been applied to these elementary systems in order to determine an effective dielectric constant for each sublayer. The representation of a thin film by an equivalent matrix \( M(d) \), developed by Abelès [21] has then been used. The matrix vector \( A(D) \) containing the amplitudes of the electric and magnetic fields \( E \) and \( H \) at the exit of the whole coating (multilayer system) has been calculated versus the corresponding matrix vector \( A(0) \) at the entrance by multiplying the equivalent matrices relative to the sublayers constituting the coating:

\[
[A(0)] = [M_1(z_1)] [M_2(z_2)] \cdots [M_n(z_n)] [A(D)]
\]

with

\[
[A(z)] = \begin{bmatrix} E(z) \\ H(z) \end{bmatrix}
\]

\[
[M_i(z)] = \begin{bmatrix} \cos \beta_i & i g_i \sin \beta_i \\ i g_i \sin \beta_i & \cos \beta_i \end{bmatrix}
\]

and

\[
g_i = (\varepsilon_i / \mu_i)^{1/2}, \quad \beta_i = k d_i = (2 \pi / \lambda) \times (\varepsilon_i / \mu_i)^{1/2}, d_i
\]

where:
- \( \varepsilon_i \) is the complex dielectric constant of the \( i \)th layer,
- \( \mu_i \) its relative permeability (equal to 1 in our problem),
- \( d_i \) its thickness, \( D \) the whole thickness of the coating,
- \( \lambda \) the wavelength of the radiation,
- \( E(z) \) and \( H(z) \) the amplitude of the electric and magnetic field at thickness \( z \).

Using the Fresnel equations, it is possible to calculate the transmissivity and the reflectivity of the whole coating as well as the reflectivity of this system deposited on a bulk substrate of known dielectric constant.

Let us now examine in detail the treatments applied to the different parts of the coating:
- the effect of the external roughness has been taken into account by including in the inhomogeneous theories a filling factor \( q \) corresponding to the volume ratio of oxide to oxide + air. This ratio depends on roughness geometry. In order to reproduce the results of scanning microscopy of the surface, we have represented the surface geometry by cones or spheres with base diameter or diameter equal to the measured period of the roughness. The filling factor of the \( N \)th sublayer expressing the ratio of the volume of the truncated cone (or sphere) in the \( N \)th sublayer \( (V_n) \) to the volume of the corresponding cylinder \( (V) \) is given by:

\[
q(N) = \frac{3 N^2 - 3 N + 1}{3 N_n^2}
\]

for a conical roughness (Fig. 7)

\[
q(N) = - N^2 + N(1 + 2 N_n) + N_n - 1/3
\]

for a spherical roughness, where \( N_n \) is the total number of sublayers. The dielectric constant of Cr₂O₃ has been assumed to be real and constant over the whole spectral range and equal to 2.3. In agreement with the results of figure 5, we have initially neglected light scattering effects;
- in the second part, the dielectric constant of chromium inclusions has been taken equal to the values given by Johnson and Christy [22] (for the range 0.32 to 0.5 μm) and Barker and Ditzenberger [23] (for the range 0.5 to 15 μm). The assumption of spherical inclusions seems to follow at best the results of electron microscopy;
- the same assumption has been used to take into account the effect of the small roughness observed for the nickel thick film deposited on the copper substrate in the case of samples 2;
— the optical constants of copper [24] and nickel [25] were determined in our laboratory on thin films evaporated and annealed under ultra-high vacuum.

5. Results and discussion. — Let us examine now the optical behaviour of each part of the coating (defined in § 4) as deduced from the model used for this part:

— figures 8a and 8b show the variations throughout the coating of the complex refractive index \((n - ik)\) calculated with the different theories, at two wavelengths: 0.54 and 13.5 \(\mu\)m. The effect of roughness

![Diagram](image-url)

**Fig. 8.** — Complex index \((n - ik)\) variations inside the coating versus thickness and corresponding values of the filling factor \(q\): a) at \(\lambda = 0.54\ \mu\)m for three models: MG (1) : Cr inclusions in \(\text{Cr}_2\text{O}_3\) matrix, MG (2) : \(\text{Cr}_2\text{O}_3\) inclusions in Cr matrix, EMT : effective medium theory; b) at \(\lambda = 13.5\ \mu\)m for two models: C.C.C.A. : Maxwell Garnett as modified by Cohen et al., EMT : effective medium theory.
in 1000 Å rough Cr$_2$O$_3$ layer is to gradually adapt the impedance of the system from air to the deeper layers. There is no absorption and the real part $n$ of the complex refractive index varies slowly from 1 ($n_{\text{air}}$) to 2.3 ($n_{\text{Cr}_2\text{O}_3}$). This layer then behaves optically like an antireflection coating on the top of the cermet. The roughness shape (conical or spherical) only modifies the slope of the $n$ profile.

---

over the second part of the coating: cermet Cr/Cr$_2$O$_3$, the $k$ values are the same in the visible (Fig. 8a) with the three theories: Maxwell Garnett with Cr inclusions in a Cr$_2$O$_3$ matrix (MG1), Maxwell Garnett with Cr$_2$O$_3$ inclusions in a Cr matrix (MG2) and Effective Medium Theory (EMT). The $n$ values are somewhat more different but they also exhibit comparable profiles.

---

Fig. 9. — Calculated values of the transmittivity $T$, reflectivity $R$, absorptivity $A$ and $A/(1 - R)$ and $T/(1 - R)$ for the isolated black chromium coating using: a) Maxwell Garnett model; b) C.C.C.A. model; c) EMT model.
The corresponding behaviours of the reflectivity of the coating alone (Figs. 9a, 9b, 9c) are comparable in the visible range. Large discrepancies appear only in the infrared, due to the fact that Maxwell Garnett theory always leads to a dielectric behaviour, while EMT leads to a percolation threshold for \( q_c \approx 0.33 \); these dielectric and quasi-metallic behaviours are indeed very different in the infrared. The differences can also be seen in figure 8b where the \( n \) and \( k \) values at \( \lambda = 13.5 \mu m \) have been plotted for C.C.C.A. theory (i.e. MG formulae reversed here at \( q_c = 0.28 \) in order to optimize the fitting) and EMT theory. The results of the classical MG theory have not been plotted, because they lead to very small \( k \) values (a few hundredths) and \( n \) values varying slowly around 2.3. Percolation effects are clearly visible for both C.C.C.A. and EMT models around the threshold (respectively \( q_c = 0.28 \) and \( q_c = 0.33 \)) : \( n \) has a discontinuity of slope while \( k \) increases suddenly by about three orders of magnitude. These results are summarized in Table I which gives the dielectric constant values calculated below and above \( q_c \) in the visible and in the infrared with the different theories.

The values of the reflectivity \( R \), transmittivity \( T \) and absorptivity \( A \) of the isolated coating (without substrate) well reflect the differences in the optical constants. These values have been plotted on figures 9a, 9b, 9c, for the three theories presented above. In order to eliminate the effect of reflections at the interfaces between the layers, inducing interference fringes in \( A \) and \( T \), we have also calculated the quantities \( A/(1 - R) \) and \( T/(1 - R) \) which better characterize intrinsic effects occurring in the coating. C.C.C.A. and EMT theories are comparable in the sense that the coating exhibits by itself (without

Table I. — Calculated values of the complex dielectric constant \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) of the black chromium coating at two thicknesses corresponding to two values of \( q \), below and above \( q_c \), at two wavelengths, using the three theories.

<table>
<thead>
<tr>
<th>( q )</th>
<th>0.25</th>
<th>0.55</th>
<th>0.25</th>
<th>0.55</th>
<th>0.25</th>
<th>0.55</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda = 0.54 \mu m )</td>
<td>( \varepsilon_1 = 7.2 )</td>
<td>( \varepsilon_1 = 7 )</td>
<td>( \varepsilon_1 = 7.2 )</td>
<td>( \varepsilon_1 = 2 )</td>
<td>( \varepsilon_1 = 6.1 )</td>
<td>( \varepsilon_1 = 3.5 )</td>
</tr>
<tr>
<td>( \varepsilon_2 = 4.5 )</td>
<td>( \varepsilon_2 = 13 )</td>
<td>( \varepsilon_2 = 4.5 )</td>
<td>( \varepsilon_2 = 9 )</td>
<td>( \varepsilon_2 = 4.1 )</td>
<td>( \varepsilon_2 = 9.5 )</td>
<td></td>
</tr>
<tr>
<td>( \lambda = 1.35 \mu m )</td>
<td>( \varepsilon_1 = 9 )</td>
<td>( \varepsilon_1 = 30 )</td>
<td>( \varepsilon_1 = 9 )</td>
<td>( \varepsilon_1 = -225 )</td>
<td>( \varepsilon_1 = 12 )</td>
<td>( \varepsilon_1 = -180 )</td>
</tr>
<tr>
<td>( \varepsilon_2 = 0.5 )</td>
<td>( \varepsilon_2 = 0.8 )</td>
<td>( \varepsilon_2 = 0.5 )</td>
<td>( \varepsilon_2 = 272 )</td>
<td>( \varepsilon_2 = 0.46 )</td>
<td>( \varepsilon_2 = 220 )</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 10. — Calculated values of the reflectivity of a black chromium coating deposited on Cu (—o—–) or Ni (—+—) using the Maxwell Garnett model, compared to the experimental measurements of the real coating on Cu (—–) and reflectivities of bulk Cu (—o—–) and Ni (—+—).

Fig. 11. — Calculated reflectivities, using the C.C.C.A. model, of the part of the coating with \( q < q_c \) deposited on bulk Cr (—o—–) and of the part of the coating with \( q > q_c \) (————) compared to the reflectivity of bulk Cr (—o—–).
substrate) selective properties: high values of \(A/(1-R)\) in the visible and the infrared, high visible and low infrared total absorptivity \(A\) (including reflections at the interfaces). EMT theory predicts a low transmittivity while this quantity is almost zero with C.C.C.A. theory; more generally, the slope of the calculated quantity variations is steeper with the C.C.C.A. theory. On the other hand, the MG theory does not predict selective optical properties for the isolated coating. If \(A/(1-R)\) exhibits a good variation pro-

Fig. 12. — Calculated values of the reflectivity of the black chromium coating deposited on Cu, assuming conical surface roughness (---Δ---) or spherical roughness (-----o-----) compared to the reflectivity measured on the real coating (---): a) calculation with the Maxwell Garnett model; b) calculation with the C.C.C.A. model; c) calculation with the EMT model.
file, \( T/(1 - R) \) is extremely high in the infrared, thus allowing the substrate to play its own part as an infrared reflector. Figure 10 shows this clearly in the case of two different substrates (nickel and copper) supporting the same coating: the total reflectivity of the coating + the substrate calculated with MG theory is almost the same in the visible, while it is notably different in the infrared, following the respective reflectivities of the metallic substrates. This result is inconsistent with the measurements which we performed on coatings deposited on bare copper or nickel plated copper (Fig. 6). The slight differences observed in the measured infrared reflectivities of these two types of samples are much smaller than the large differences in bulk IR reflectivities of Ni and Cu.

In order to show which part of the inhomogeneous system treated with the C.C.C.A. or EMT theories plays in the infrared reflectivity the same role as the substrate in the MG theory, we have calculated (Fig. 11) with the C.C.C.A. theory, the reflectivity of the part corresponding to \( q < q_c \) (with dielectric behaviour) directly deposited on bulk Cr and the reflectivity of the part corresponding to \( q > q_c \). The infrared behaviour of these two parts is almost the same, thus confirming that the part of the coating acting as an infrared reflector is the inhomogeneous medium with \( q > q_c \).

In conclusion, if one compares the reflectivity of the whole sample, calculated with the MG, C.C.C.A. (\( q_c = 0.28 \)) and EMT theories, to the measured hemispherical reflectivity (Figs. 12a, 12b, 12c), one can say that:

- the only effect of a change of shape of the external roughness is a wavelength shift of the interference fringe system occurring in that part of the coating which presents a dielectric-like behaviour, i.e. the whole coating with the MG theory, that part of the coating where \( q < q_c \) with the C.C.C.A. and EMT theories. In other words, this change is equivalent to a thickness change of the dielectric layer;

- with all theories, the calculated reflectivity is always greater than of the measured hemispherical by about 5\% in the visible range. This can be partly explained by the weak light scattering observed for the real samples (cf. § 3.3), which has not been taken into account in the models; each model considers the upper dielectric part of the coating as a thin plane parallel film which, besides, induces interference fringes in the calculated reflectivity, which do not exist for the real coating;

- the slope corresponding to the cut-off wavelength is best reproduced with EMT theory but its position is at too low a wavelength. The best agreement is obtained with C.C.C.A. theory. The cut-off wavelength has been fitted in this case by modifying the \( q_c \) value \( (q_c = 0.28) \) at which the MG formulae are inverted (cf. Fig. 13). One can notice that in EMT theory the critical value of the filling factor is roughly equal to the depolarization factor \( g \). Our assumption of spherical inclusions \( (g = 1/3) \) leads thus to a \( q_c \) value around 0.3. Other assumptions on the roughness shape would lead to other \( g \), i.e. \( q_c \), values which would allow a better fit to the experimental results but without any physical meaning. C.C.C.A. theory gives also the best agreement between calculated and measured values of the infrared reflectivity; MG theory has been proved to be inconsistent with experiment in this range;

- one can finally notice that the limits of applicability of EMT theory mentioned in § 2.3

\[
\left( \frac{1}{20} < \frac{\delta_l}{\delta_m} < 20 \right)
\]

do not appear clearly in our results presented in figure 12c.

6. Conclusion. — We have presented a detailed comparison between inhomogeneous medium theories as applied to the calculation of the optical properties of black chromium. The Maxwell Garnett formalism is unable to reproduce the experimental results. The Maxwell Garnett theory as modified by Cohen et al. [15] and Bruggeman's effective medium theory give a much better agreement. They well describe the threshold observed around 2.5 \( \mu \)m in the spectral reflectivity, which can be directly related to the conduction percolation threshold of the coating, occurring at a critical Cr filling factor \( q_c \). This value can be directly adjusted in C.C.C.A. theory since it
corresponds mathematically to the value of $q$ at which the MG formula has to be inverted. In EMT theory, this value can be related to the depolarization factor, depending on the shape of the metallic inclusions. The infrared experimental values of the reflectivity are especially well reproduced with these two last theories, whereas they give too high reflectivity values in the visible. This failure of all the theories in the visible range is certainly due to the fact that one does not take into account light scattering due to external surface roughness and that the coating is considered to be plane parallel film.

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References